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(54)【発明の名称】

アントラセン系化合物、その製造方法および有機電界発光素子

(54) [Title of Invention]

MANUFACTURING METHOD AND ORGANIC ELECTROLUMINESCENT ELEMENT OF ANTHRACENE COMPOUND ,

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Abstract

(57)【要約】

(57) [Abstract]

【課題】

[Problems to be Solved by the Invention]

耐熱性に優れ、駆動電圧が低く、しかも発光効率の高い有機電界発光素子の製造を可能にする化合物を提供する。

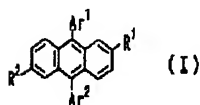
It is superior in heat resistance, drive voltage is low, furthermore compound which makes production of organic electroluminescent element where light emission efficiency is high possible is offered.

【解決手段】

[Means to Solve the Problems]

下記一般式(I)で表されるアントラセン系化合物

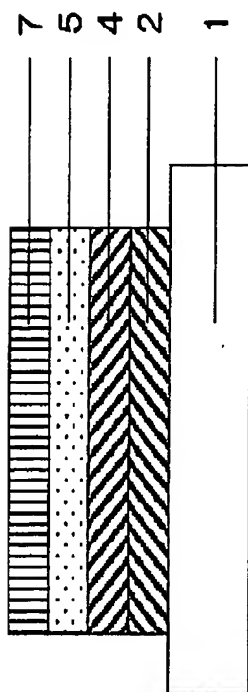
anthracene compound which is displayed with below-mentioned General Formula (I)



(式中、Ar¹ および Ar² は、それぞれ独立して置換基を有していてもよい5または6員環の、芳香族炭化水素環または芳香族複素環の単環基又は2~5の縮合環基を示し、R¹ および R² は、それぞれ独立して、3級アミノ基、5または6員環の芳香族炭化水素環または芳香族複素環の単環基又は2~5の縮合環基を示す。但し、R¹ と R² が共に3級アミノ基であることはなく、また R¹ および/または R² が3級アミノ基、芳香族炭化水素環基または芳香族複素環基を示す場合、これらは更に置換されていてもよい。)

(In Formula, Ar¹ and Ar², becoming independent respectively, aromatic hydrocarbon ring of optionally substituted 5 or 6 members ring or monocycle basis of aromatic heterocycle or show condensed ring group of 2 - 5, R¹ and R², becoming independent respectively, condensed ring group of aromatic hydrocarbon ring of tertiary amino group, 5 or 6 members ring or monocycle basis or show 2 of aromatic heterocycle - 5. However, R¹ and R² together not to be times when it is a tertiary amino group, in addition when R¹ and/or R² show tertiary amino group, aromatic

R² shows tertiary amino group, aromatic hydrocarbon ring group or heteroaromatic group, as for these furthermore optionally substitutable.)



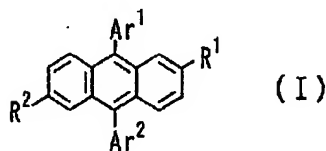
Claims

【特許請求の範囲】

【請求項 1】

下記一般式(I)で表されるアントラセン系化合物

【化 1】



(式中、Ar¹ および Ar² は、それぞれ独立して置換基を有していてもよい5または6員環の、芳香族炭化水素環または芳香族複素環の単環基又は2~5の縮合環基を示す。R¹ および R² のうち、一方は5または6員環の芳香族炭化水素環または芳香族複素環の単環基または2~5縮合環基を表し、他方は、5または6員環の芳香族炭化水素環または芳香族複素環の単環基または2~5縮合環基を表すか、または3級アミノ基を表

[Claim(s)]

[Claim 1]

anthracene compound which is displayed with below-mentioned General Formula (I)

[Chemical Formula 1]

(In Formula, Ar¹ and Ar², becoming independent respectively, condensed ring group of aromatic hydrocarbon ring of optionally substituted 5 or 6 members ring or monocycle basis or show 2 of aromatic heterocycle - 5. Inside R¹ and R², on one hand you display aromatic hydrocarbon ring of 5 or 6 members rings or monocycle basis or 2 - 5 condensed ring group of aromatic heterocycle, other displays aromatic hydrocarbon ring of 5 or 6 members rings, or or monocycle

す。なお、 R^1 および/または R^2 が 3 級アミノ基、芳香族炭化水素環基または芳香族複素環基を示す場合、これらは更に置換されていてもよい。)

【請求項 2】

前記一般式(I)において、 Ar^1 および Ar^2 が、それぞれ独立して置換基を有していてもよいフェニル基、ナフチル基、アントリル基、カルバゾリル基、チエニル基、ピリジル基から選ばれることを特徴とする請求項 1 記載のアントラセン系化合物。

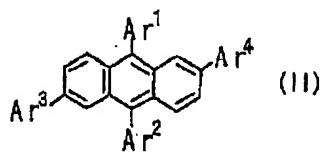
【請求項 3】

前記一般式(I)において、 R^1 および R^2 がそれぞれ独立して、3 級アミノ基、フェニル基、ナフチル基、アントリル基、ビフェニル基およびカルバゾリル基から選ばれ、これらは更に置換基を有していてもよいことを特徴とする請求項 1 または 2 記載のアントラセン系化合物。

【請求項 4】

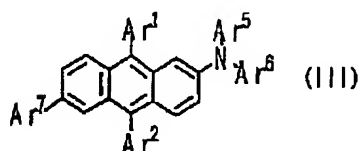
上記一般式(I)で表される化合物が、下記一般式(II)または(III)のいずれかで表されることを特徴とする、請求項 1 ないし 3 のいずれかに記載のアントラセン系化合物。

【化 2】



(式中、 Ar^1 から Ar^4 は、各々独立して、置換基を有していても良い 5 又は 6 員環の芳香族炭化水素環または芳香族複素環の単環基又は 2~5 の縮合環基を表す)

【化 3】



(式中、 Ar^1 、 Ar^2 、 Ar^3 から Ar^7 は、各々独立して、置換基を有していても良い 5 又は 6 員環の芳香

basis or 2 - 5 condensed ring group of aromatic heterocycle displays tertiary amino group . Furthermore, when $R^{¹}$ and/or $R^{²}$ shows tertiary amino group , aromatic hydrocarbon ring group or heteroaromatic group , as for these furthermore optionally substitutable .)

[Claim 2]

In aforementioned General Formula (I) , $Ar^{¹}$ and $Ar^{²}$ becoming independent, respectively, anthracene compound . which is stated in the Claim 1 which is chosen from optionally substituted phenyl group , naphthyl group , anthryl group , carbozoyl group , thienyl group , pyridyl group and makes feature

[Claim 3]

In aforementioned General Formula (I) , $R^{¹}$ and $R^{²}$ becoming independent respectively, anthracene compound . which is stated in Claim 1 or 2 which is chosen from tertiary amino group , phenyl group , naphthyl group , anthryl group , biphenyl group , and carbozoyl group as for these furthermore optionally substituted it makes feature

[Claim 4]

compound which is displayed with above-mentioned General Formula (I) , is displayed with any of below-mentioned General Formula (II) or (III) , the anthracene compound . which it makes feature, states in any of the Claims 1 through 3

[Chemical Formula 2]

(In Formula, $Ar^{⁴}$, independently, condensed ring group of aromatic hydrocarbon ring of 5 or 6-member ring which are good having possessed substituent or monocycle basis or displays 2 of aromatic heterocycle - 5 from $Ar^{¹}$.)

[Chemical Formula 3]

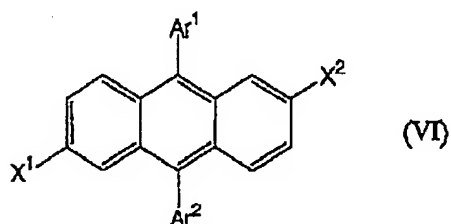
(In Formula, $Ar^{⁷}$, independently, condensed ring group of aromatic hydrocarbon ring of 5 or 6-member ring

族炭化水素環または芳香族複素環の単環基又は 2~5 の縮合環基を表す)

【請求項 5】

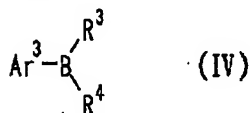
下記一般式(VI)で表されるアントラセン誘導体

【化 4】

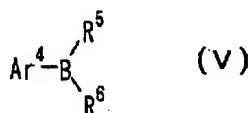


(式中、X¹ および X² は各々独立にハロゲン原子を表し、Ar¹ および Ar² は前記一般式(I)におけると同義である。)を、下記一般式(IV)及び(V)で表される芳香族ホウ素誘導体

【化 5】



【化 6】



(式中、R³~R⁶ は水酸基または置換基を有しているもよいアルコキシ基を示し、R³ と R⁴、R⁵ と R⁶ は結合して環を形成しても良い。Ar³ 及び Ar⁴ はそれぞれ独立して置換基を有しているもよい 5 又は 6 員環の芳香族炭化水素環または芳香族複素環の単環基又は 2~5 の縮合環基を表す。)と反応させることを特徴とする、上記一般式(II)で示されるアントラセン系化合物の製造方法。

【請求項 6】

少なくとも、請求項 1 ないし 5 のいずれかに記載のアントラセン系化合物を含有する層を有する

which are good having possessed substituent or monocycle basis or displays 2 of aromatic heterocycle - 5 from Ar¹, Ar², Ar⁵.)

[Claim 5]

anthracene derivative which is displayed with below-mentioned General Formula (VI)

[Chemical Formula 4]

aromatic boron derivative which is displayed (In Formula, X¹ and X² display halogen atom in each independence, Ar¹ and Ar² when in aforementioned General Formula (I), are synonymous.), with below-mentioned General Formula (IV) and (V)

[Chemical Formula 5]

[Chemical Formula 6]

manufacturing method of anthracene compound which (In Formula, R³~R⁶ shows hydroxy group or optionally substituted alkoxy group, R³ and R⁴, R⁵ and R⁶ connecting, are good forming ring. Ar³ and Ar⁴ becoming independent respectively, aromatic hydrocarbon ring of optionally substituted 5 or 6-member ring or monocycle basis of aromatic heterocycle or display condensed ring group 2 - 5.) with it reacts it makes feature, is shown with above-mentioned General Formula (II)

[Claim 6]

At least, it possesses layer which contains anthracene compound which is stated in any of Claims 1 through 5 it

ことを特徴とする、有機電界発光素子。

【請求項 7】

有機電界発光素子が、対向する陽極と陰極との間に発光層を有し、請求項 1 ないし 5 のいずれかに記載のアントラセン系化合物を含有する層を、該発光層と陽極との間に有することを特徴とする、請求項 6 に記載の有機電界発光素子。

【請求項 8】

有機電界発光素子が、対向する陽極と陰極との間に発光層を有し、請求項 1 ないし 5 のいずれかに記載のアントラセン系化合物を含有する層を、該発光層として有することを特徴とする、請求項 6 に記載の有機電界発光素子。

Specification

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は有機電界発光素子に関するものであり、詳しくは、有機化合物からなる発光層に電界をかけて光を放出する薄膜型デバイスにおいて、特定構造のアントラセン系化合物を含む層を有する有機電界発光素子、および該アントラセン系化合物とその製造方法に関するものである。

【0002】

【従来の技術】

従来、薄膜型の電界発光(EL)素子としては、無機材料の II-VI 族化合物半導体である ZnS、CaS、SrS 等に、発光中心である Mn や希土類元素(Eu、Ce、Tb、Sm 等)をドーピングしたものが一般的であるが、上記の無機材料から作製した EL 素子は、

- 1) 交流駆動が必要(一般に 50~1000Hz)、
 - 2) 駆動電圧が高い(一般に~200V 程度)、
 - 3) フルカラー化が困難(特に青色に問題がある)、
 - 4) 周辺駆動回路のコストが高い、
- という問題点を有している。

makes feature, the organic electroluminescent element .

[Claim 7]

organic electroluminescent element . where organic electroluminescent element , has light emitting layer between anode and the cathode which oppose it possesses layer which contains anthracene compound which is stated in any of Claims 1 through 5 , between said light emitting layer and anode makes feature, states in Claim 6

[Claim 8]

organic electroluminescent element , has light emitting layer between anode and cathode which opposeas said light emitting layer possesses layer which contains anthracene compound whichis stated in any of Claims 1 through 5 , organic electroluminescent element . which it makesfeature, states in Claim 6

[Description of the Invention]

[0001]

[Technological Field of Invention]

As for this invention being something regarding organic electroluminescent element , as for details,applying electric field on light emitting layer which consists of organic compound , it is a organic electroluminescent element , and a said anthracene compound and regarding manufacturing method something whichpossess layer which includes anthracene compound of specific structure in thin film type device which discharges light.

[0002]

[Prior Art]

Until recently, in ZnS , Ca S, SrS etc which is a II-Group VI compound semiconductor of inorganic material as the electroluminescence (EL) element of thin film type , those which Mn and rare earth element (Eu, Ce, Tb, Sm etc)which are a light emitting center dope are done are general, but as for EL device which is produced from above-mentioned inorganic material ,

- 1) alternating current drive necessity (Generally 50 - 1000 Hz),
 - 2) drive voltage is high, (Generally - 200 Vextent),
 - 3) making full color difficulty (There is a problem in especially blue .),
 - 4) Cost of periphery drive circuit is high,
- With it has possessed problem which is said.

【0003】

しかし、近年、上記問題点の改良のため、有機薄膜を用いた EL 素子の開発が行われるようになった。

特に、発光効率を高めるため、電極からのキャリア注入の効率向上を目的として電極の種類の最適化を行い、芳香族ジアミンからなる正孔輸送層と 8-ヒドロキシキノリンのアルミニウム錯体からなる発光層とを設けた有機電界発光素子の開発(Appl. Phys. Lett., 51 巻, 913 頁, 1987 年)により、従来のアントラセン等の単結晶を用いた EL 素子と比較して発光効率の大幅な改善がなされている。

また、例えば、8-ヒドロキシキノリンのアルミニウム錯体をホスト材料として、クマリン等のレーザー蛍光色素をドーピングすること(J. Appl. Phys., 65 巻, 3610 頁, 1989 年)で、発光効率の向上や発光波長の変換等も行われている。

【0004】

上記の様な低分子材料を用いた電界発光素子の他にも、発光層の材料として、ポリ(p-フェニレンビニレン)、ポリ[2-メトキシ-5-(2-エチルヘキシルオキシ)-1,4-フェニレンビニレン]、ポリ(3-アルキルチオフェン)等の高分子材料を用いた電界発光素子の開発や、ポリビニルカルバゾール等の高分子に低分子の発光材料と電子移動材料を混合した素子の開発も行われている。

【0005】

【発明が解決しようとする課題】

有機電界発光素子をフラットパネル・ディスプレイ等の表示素子に応用するためには、優れた耐熱性、低駆動電圧、高発光効率などが要求される。

その中で、本発明者らは発光効率の向上につき鋭意検討した結果、特定構造のアントラセン系化合物が有効であることを見出し、本発明に至った。

【0006】

【課題を解決するための手段】

本発明者等は、上記課題を解決するため鋭意検討を重ね、9、10-位に芳香族基を有し、かつ

【0003】

But, recently, for improving above-mentioned problem, it reached the point where development of EL device which uses organic thin film is done.

Especially, in order to raise light emission efficiency, optimization of types of the electrode is done with efficiency improvement of carrier fill from the electrode as objective, large improvement of light emission efficiency has done by comparison with EL device which uses conventional anthracene or other single crystal with development (Applied Physics Letters, Vol. 51, 913 page, 1987) of organic electroluminescent element which provides light emitting layer where positive hole transport layer and 8-hydroxy quinoline where it consists of aromatic diamine consist of aluminum complex.

In addition, dope is done with thing (Journal of Applied Physics (0021 - 8979, JAPIAU), 6 Vol. 5, 3610 page, 1989) which, also improvement of light emission efficiency and conversion etc of light emitting wavelength are done the fluorescent pigment for coumarin or other laser with aluminum complex of for example 8-hydroxy quinoline as host material.

【0004】

Above-mentioned way to other than electroluminescent element which uses low molecular weight material, poly (p-phenylene vinylene), poly [2-methoxy-5-(2-ethylhexyloxy)-1 and 4-phenylene vinylene], also light-emitting material of low molecular weight and development of element which mixes electron transfer material are done in development and poly vinyl carbazole or other polymer of electroluminescent element which uses poly (3-alkyl thiophene) or other polymeric material as material of light emitting layer.

【0005】

【Problems to be Solved by the Invention】

In order to apply organic electroluminescent element to flat panel * display or other display element, heat resistance, low drive voltage, high light emission efficiency etc which is superior is required.

Among those, these inventors result of diligent investigation, anthracene compound of the specific structure is effective concerning improvement of light emission efficiency, you discovered, reached to this invention.

【0006】

【Means to Solve the Problems】

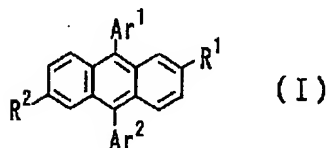
this inventor etc, in order to solve above-mentioned problem, diligent investigation is repeated, 9 and 10 - aromatic group

2、6-位に特定の置換基を導入した新規なアントラセン系化合物が、優れた性能を有することを見出し本発明を達成した。

即ち、本発明の要旨は、下記一般式(I)で表されるアントラセン系化合物

【0007】

【化 7】



【0008】

(式中、Ar¹ および Ar² は、それぞれ独立して置換基を有していてもよい5または6員環の、芳香族炭化水素環または芳香族複素環の単環基又は2~5の縮合環基を示す。R¹ および R² のうち、一方は5または6員環の芳香族炭化水素環または芳香族複素環の単環基または2~5縮合環基を表し、他方は、5または6員環の芳香族炭化水素環または芳香族複素環の単環基または2~5縮合環基を表すか、または3級アミノ基を表す。なお、R¹ および/または R² が3級アミノ基、芳香族炭化水素環基または芳香族複素環基を示す場合、これらは更に置換されていてもよい。)この製造方法およびこれを含有する層を有することを特徴とする有機電界発光素子に存する。

【0009】

【発明の実施の形態】

以下、本発明を詳細に説明する。

本発明の化合物は前記一般式(I)で示される構造を有するものであって、2、6位および9、10位が置換されていることに特徴がある。

一般式(I)において Ar¹ 及び Ar² は、それぞれ独立して、置換基を有していてもよい5又は6員環の、芳香族炭化水素環または芳香族複素環の単環基又は2~5の縮合環基を示す。

好ましくは5または6員環の芳香族炭化水素環または芳香族複素環の、単環基または2~3の

possesses in rank, at same time 2 and 6 - novel anthracene compound which introduces specific substituent into rank, has performance which is superior, you discovered and achieved this invention .

Namely, as for gist of this invention , anthracene compound which is displayed with below-mentioned General Formula (I)

[0007]

[Chemical Formula 7]

[0008]

It exists in organic electroluminescent element which (In Formula, Ar¹ and Ar², becoming independent respectively, condensed ring group of aromatic hydrocarbon ring of optionally substituted 5 or 6 members ring or monocycle basis or show 2 of aromatic heterocycle - 5. Inside R¹ and R², on one hand you display aromatic hydrocarbon ring of 5 or 6 members rings or monocycle basis or 2 - 5 condensed ring group of aromatic heterocycle , other displays aromatic hydrocarbon ring of 5 or 6 members rings, or or monocycle basis or 2 - 5 condensed ring group of aromatic heterocycle displays tertiary amino group . Furthermore, when R¹ and/or R² shows tertiary amino group , aromatic hydrocarbon ring group or heteroaromatic group , as for these furthermore optionally substitutable .) possesses this manufacturing method and layer which contains this and makes feature.

[0009]

[Embodiment of the Invention]

Below, this invention is explained in detail.

As for compound of this invention being something which possesses the structure which is shown with aforementioned General Formula (I), there is a feature in 2 and 6 rank and 9 and 10 rank being substituted.

Ar¹ and Ar², becoming independent respectively, aromatic hydrocarbon ring of optionally substituted 5 or 6-member ring or monocycle basis of aromatic heterocycle or show condensed ring group 2 - 5 in the General Formula (I).

aromatic hydrocarbon ring of preferably 5 or 6 members ring or, monocycle basis of aromatic heterocycle or with

縮合環基であり、中でもフェニル基、ナフチル基、アントリル基、ピリジル基、チエニル基、カルバゾリル基が好ましい。

特に好ましくは、フェニル基、ナフチル基またはカルバゾリル基である。

[0010]

Ar¹ および Ar² が有する置換基としては、ハロゲン原子;メチル基、エチル基等の炭素数 1~6 のアルキル基;ビニル基等の炭素数 2~7 のアルケニル基;メトキシ基、エトキシ基等の炭素数 1~6 のアルコキシ基;メトキシカルボニル基、エトキシカルボニル基等の炭素数 2~7 のアルコキシカルボニル基;フェノキシ基、ベンジルオキシ基などのアリールオキシ基;ジエチルアミノ基、ジイソプロピルアミノ基等のジアルキルアミノ基;ジフェニルアミノ基、フェニルナフチルアミノ基等のジアリールアミノ基;ジベンジルアミノ基、ジフェネチルアミノ基などのジアルキルアミノ基等が挙げられる。

R¹ および R² は各々独立に、3級アミノ基、あるいは 5 または 6 員環の芳香族炭化水素環または芳香族複素環の、単環基又は 2~5 の縮合環基を示す。

但し R¹ および R² のうち少なくとも一方は、上記単環基又は 2~5 の縮合環基である。

[0011]

3 級アミノ基としては、ジメチルアミノ基、ジエチルアミノ基、ジフェニルアミノ基、フェニルナフチルアミノ基など炭素数 1~7 のアルキル基やアリール基を有するものが挙げられ、特に好ましくはアリールアミノ基が挙げられる。

芳香族炭化水素基として、好ましくは 5 または 6 員環の芳香族炭化水素環または芳香族複素環の、単環基または 2~3 の縮合環基が挙げられ、中でも特にフェニル基、ナフチル基、アントリル基などが好ましい。

[0012]

芳香族複素環基として、好ましくは 5 または 6 員環の芳香族炭化水素環または芳香族複素環の、単環基または 2~3 の縮合環基が挙げられ、中でも特にピリジル基、キノリル基、チエニル基、カルバゾリル基などが好ましい。

上記の R¹ および R² が 3 級アミノ基、芳香族炭化水素環または芳香族複素環基である場合、これらは更に置換されていてもよい。

condensed ring group 2 -3, phenyl group , naphthyl group , anthryl group , pyridyl group , thienyl group , carbozoyl group is desirable even among them.

It is a particularly preferably , phenyl group , naphthyl group or a carbozoyl group .

[0010]

You can list alkoxy carbonyl group ;phenoxy group , benzyloxy group or other aryloxy group ;diethyl amino group , diisopropylamino group or other dialkyl amino group ;diphenylamino group , phenyl naphthyl amino group or other diaryl amino group ;dibenzyl amino group , di phenethyl amino group or other di aralkyl amino group etc of alkoxy group ;methoxycarbonyl group , ethoxy carbonyl group or other carbon number 2~7 of alkenyl group ;methoxy group , ethoxy group or other carbon number 1~6 of alkyl group ;vinyl group or other carbon number 2~7 of halogen atom ;methyl group , ethyl group or other carbon number 1~6 as substituent which Ar¹ and Ar² can possess.

R¹ and R² in each independence, tertiary amino group , or aromatic hydrocarbon ring of 5 or 6-member ring or, monocycle basis of aromatic heterocycle or show condensed ring group 2 - 5.

However inside at least one of R¹ and R² above-mentioned monocycle basis or is condensed ring group 2 - 5.

[0011]

As tertiary amino group , alkyl group of carbon number 1~7, and those which such as dimethylamino group , diethyl amino group , diphenylamino group , phenyl naphthyl amino group , possess aryl group you can list can list particularly preferably aryl amino group .

As aromatic hydrocarbon group , aromatic hydrocarbon ring of preferably 5 or 6 members ring or, monocycle basis of aromatic heterocycle or you can list condensed ring group 2 - 3, especially phenyl group , naphthyl group , anthryl group etc is desirable even among them.

[0012]

As heteroaromatic group , aromatic hydrocarbon ring of preferably 5 or 6 members ring or, monocycle basis of aromatic heterocycle or you can list condensed ring group 2 - 3, especially pyridyl group , quinolyl group , thienyl group , carbozoyl group etc is desirable even among them.

When above-mentioned R¹ and R² are tertiary amino group , aromatic hydrocarbon ring group or the heteroaromatic group , as for these furthermore optionally substitutable .

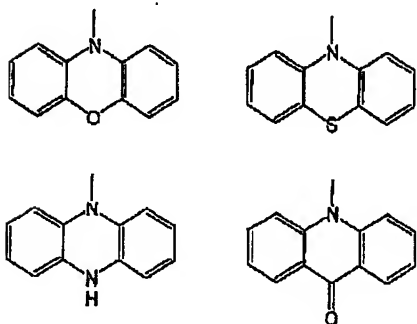
【0013】

このような置換基としてはハロゲン原子、アルキル基、アルコキシ基、アリールオキシ基、アリールアミノ基、アルキルアミノ基、芳香族炭化水素基、芳香族複素環基などが挙げられる。

該アリールアミノ基においては、窒素原子に結合する 2 つのアリール基が互いに結合し、非芳香族性の環を形成していても良く、このような例としては、例えば

【0014】

【化 8】



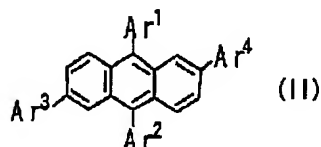
【0015】

等が挙げられる。

一般式(I)で表される化合物として、より具体的には下記一般式(II)または(III)のいずれかで表される化合物が挙げられる。

【0016】

【化 9】



【0017】

(式中、Ar¹ から Ar⁴ は、各々独立して、置換基を有していても良い 5 又は 6 員環の芳香族炭化水素環または芳香族複素環の単環基又は 2~5 の縮合環基を表す)

【0018】

【化 10】

【0013】

You can list halogen atom , alkyl group , alkoxy group , aryloxy group , aryl amino group , alkyl amino group , aromatic hydrocarbon group , heteroaromatic group etc as this kind of substituent .

Regarding said aryl amino group , 2 aryl group which are connected to nitrogen atom to connect be good forming nonaromatic ring mutually, as this kind of example, for example

【0014】

[Chemical Formula 8]

【0015】

Such as is listed.

You can list compound which is displayed more concretely with the any of below-mentioned General Formula (II) or (III) as compound which is displayed with General Formula (I).

【0016】

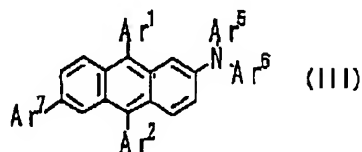
[Chemical Formula 9]

【0017】

(In Formula, Ar¹ to Ar⁴, independently, condensed ring group of aromatic hydrocarbon ring of 5 or 6-member ring which are good having possessed substituent or monocycle basis or displays 2 of aromatic heterocycle - 5 from Ar¹ to Ar⁴.)

【0018】

[Chemical Formula 10]



【0019】

(式中、Ar¹ から Ar⁷ は、各々独立して、置換基を有していても良い 5 又は 6 員環の芳香族炭化水素環または芳香族複素環の単環基又は 2~5 の縮合環基を表す)

【0020】

一般式(II)における Ar³ および Ar⁴ としては、一般式(I)における Ar¹ および Ar² と同様の基が挙げられ、好ましい基も同様である。

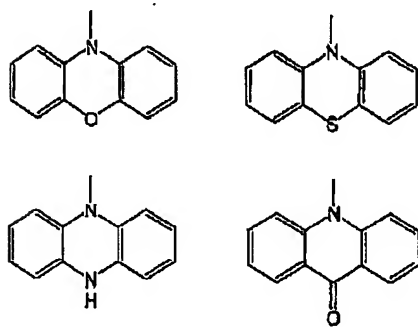
一般式(III)における Ar⁵~Ar⁷ としては、一般式(I)における Ar¹ および Ar² と同様の基が挙げられ、好ましい基も同様である。

よって、-NAr⁵Ar⁶ はジフェニルアミノ基、フェニルナフチルアミノ基など 3 級アリールアミノ基を表す。

該アリールアミノ基においては、窒素原子に結合する 2 つのアリール基が互いに結合し、非芳香族性の環を形成していても良く、このような例としては、例えば

【0021】

【化 11】



【0022】

等があげられる。

【0023】

一般式(II)における Ar³ および Ar⁴、並びに一般

【0019】

(In Formula, Ar⁷, independently, condensed ring group of aromatic hydrocarbon ring of 5 or 6-member ring which are good having possessed substituent or monocycle basis or displays 2 of aromatic heterocycle - 5 from Ar¹.)

【0020】

Also basis to which you can list group which is similar to the Ar¹ and Ar² in General Formula (I) as Ar³ and Ar⁴ in the General Formula (II), is desirable is similar.

Also basis to which you can list group which is similar to the Ar¹ and Ar² in General Formula (I) as Ar⁵~Ar⁷ in general formula (III), is desirable is similar.

Depending, -NAr⁵Ar⁶ displays ternary aryl amino group such as diphenylamino group, phenyl naphthyl amino group.

Regarding said aryl amino group, 2 aryl group which are connected to nitrogen atom to connect be good forming nonaromatic ring mutually, as this kind of example, for example

【0021】

[Chemical Formula 11]

【0022】

Such as is listed.

【0023】

It is a most preferably, aryl amino group or a N-carbozoyl

式(III)における Ar^7 が有する置換基として、最も好ましくは、アリールアミノ基または N-カルバゾリル基である。

一般式(II)および(III)で表されるこれらの化合物は、イオン化ポテンシャルが低く、正孔輸送材料として良い特性を示す。

特に、高いガラス転移温度や融点を有することは有機電界発光素子における耐熱性という重要な課題を満足する。

また、一般式(III)で表される化合物は異なった型の置換基を有する非対称な化合物であり、これにより、3級アリールアミノ基と芳香族炭化水素基の両方の特性を有する化合物を得ることが出来、所望する特性を制御することが出来る。

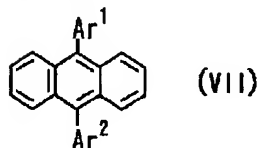
【0024】

本発明の化合物は、例えば下記に従って製造することができる。

下記一般式(VII)

【0025】

【化 12】

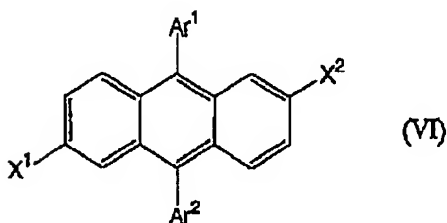


【0026】

(式中、 Ar^1 および Ar^2 は前記一般式(I)におけると同義。)で表されるアントラセン系化合物と、所望のハロゲン原子を含むハロゲン化剤を用いて下記一般式(VI)

【0027】

【化 13】



group as substituent which $Ar^{>3}</sup>$ in General Formula (II) and $Ar^{>7}</sup>$ in $Ar^{>4}</sup>$, and general formula (III) can possess.

characteristic where as for these compound which are displayed with General Formulas (II) and (III), ionization potential is low, is good making positive hole transporting material is shown.

Especially, as for possessing high glass transition temperature and melting point important problem, heat resistance in organic electroluminescent element is satisfied.

In addition, compound which is displayed with general formula (III) with the asymmetric compound which possesses substituent of type which differs, because of this, be able to acquire compound which possesses characteristic of the both of tertiary aryl amino group and aromatic hydrocarbon group, characteristic which is desired is controlled is possible.

【0024】

Following on for example description below, it can produce compound of the this invention.

Below-mentioned General Formula (VII)

【0025】

[Chemical Formula 12]

【0026】

Making use of anthracene compound which is displayed with (In Formula, as for $Ar^{>1}</sup>$ and $Ar^{>2}</sup>$ when in the aforementioned General Formula (I), synonymy.) and the halogenating agent which includes desired halogen atom below-mentioned General Formula (VI)

【0027】

[Chemical Formula 13]

【0028】

(式中、 X^1 および X^2 は各々独立にハロゲン原子を表し、 Ar^1 および Ar^2 は前記一般式(I)におけると同義である。)で表されるハロゲン原子含有アントラセン系化合物を得る。

ハロゲン化剤としては特に限定されるものではないが、所望の置換基 X (X はハロゲン原子を表す)を有する N-コハク酸イミド(J. Org. Chem., vol. 44, No.25, 4733 (1979))が好適に使用される。

ハロゲン化剤の使用量は、前記一般式(VII)で表される化合物に対し、2~10 倍モル、好ましくは 2~5 倍モル程度である。

【0029】

反応は通常、乾燥窒素やアルゴンなど不活性雰囲気下で行われる。

また、反応は通常、不活性溶媒中で実施される。

使用される不活性溶媒としては、N,N-ジメチルホルムアミド、N-メチルピロリドン、ジメチルスルホキシド、クロロベンゼン、ジクロロベンゼン、トリクロロベンゼン、ニトロベンゼン、トルエン、キシレン、メチルセロソルブ、エチルセロソルブまたは水などが挙げられるが、これらのうち、N,N-ジメチルホルムアミド、N-メチルピロリドンが好適である。

溶媒の使用量は、一般式(VII)の化合物に対して、通常、5~50 重量倍、好ましくは、10~20 重量倍が適当である。

【0030】

反応温度は 50 deg C から 200 deg C の範囲、好ましくは 50 deg C から 100 deg C、反応時間は 0.5~48 時間程度である。

反応終了後、反応液を冷却し、析出した結晶を濾過し、メタノール、アセトンまたは水で洗浄し乾燥すれば目的物が得られる。

また、冷却しても晶出しない場合には、反応液をメタノールか水に放出し、析出した結晶を濾過し、メタノールまたは水で洗浄し乾燥すれば目的物が得られる。

メタノールか水に放出しても析出しない場合には、酢酸エチル、ジクロロメタン等で抽出し、洗浄、乾燥、濃縮すれば良い。

【0028】

halogen atom-containing anthracene compound which is displayed with (In Formula, $X^{sup>1</sup>}$ and $X^{sup>2</sup>}$ display halogen atom in each independence, $Ar^{sup>1</sup>}$ and $Ar^{sup>2</sup>}$ when in aforementioned General Formula (I), are synonymous.) is obtained.

As halogenating agent it is not something which especially is limited. N- succinimide (Journal of Organic Chemistry (0022 - 3263, JOCEAH), vol. 44, No.25, 4733 (1979)) which possesses desired substituent X (X displays halogen atom .) is used for ideal.

amount used of halogenating agent is 2 - 10 times mole , preferably 2~5 times mole extent vis-a-vis compound which is displayed with aforementioned General Formula (VII).

【0029】

Reaction usually is done under inert atmosphere such as dry nitrogen and argon .

In addition, reaction usually is executed in inert solvent .

You can list N,N- dimethylformamide , N- methyl pyrrolidone , dimethyl sulfoxide , chlorobenzene , dichlorobenzene , trichlorobenzene , nitrobenzene , toluene , xylene , methyl cellosolve , ethyl cellosolve or water etc , as inert solvent which is used, but among these, N,N- dimethylformamide , N- methyl pyrrolidone is ideal.

As for amount used of solvent , usually, 5 - 50 weight multiple , preferably , 10~20weight multiple are suitable vis-a-vis compound of General Formula (VII).

【0030】

As for reaction temperature from 50 deg C range of 200 deg C, as for 100 deg C, reaction time 0.5 - 48 -hour extent is from preferably 50 deg C.

If after reaction termination , it cools reaction mixture , it filters crystal which was precipitated, washes with methanol , acetone and or water dries object compound is acquired.

In addition, cooling, when crystallization it does not do, if it discharges reaction mixture to methanol , or water it filters crystal which it precipitated, washes with methanol and or water dries object compound is acquired.

Discharging to methanol , or water it does not precipitate, when, if it extracts with ethylacetate , dichloromethane and etc washing, it dries and concentrates it is good.

生成物は必要に応じて再結晶またはカラムクロマトグラフィーにより精製することができる。

この場合、精製溶媒としては、N,N-ジメチルホルムアミド、N-メチルピロリドン、クロロベンゼン、ジクロロベンゼン、トルエン、酢酸エチル、クロロホルム、塩化メチレンなどが好適である。

【0031】

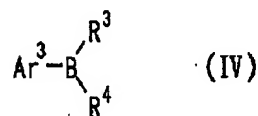
必要に応じて、前記文献における N-コハク酸イミドの N-置換基 X は、別のハロゲン原子に置き換えて良い。

例えば臭素原子をヨウ素原子に置換する反応 (Chemistry Letters, 411(1985))が挙げられる。

続いて、得られたハロゲン化合物を下記一般式 (IV)および(V)

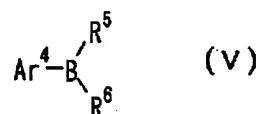
【0032】

【化 14】



【0033】

【化 15】



【0034】

(式中、Ar³ および Ar⁴ は式(II)におけると同義、R³~R⁶ は水酸基または置換基を有していてもよいアルコキシ基を示し、R³とR⁴、R⁵とR⁶は結合して環を形成しても良い。)で表される芳香族ホウ素誘導体と鈴木カップリング法 (Chem. Rev., Vol.95, 2457 (1995))にて反応させることにより、前記一般式(II)で表されるアントラセン系化合物を得る。

【0035】

また一般式(III)のように異なった型の置換基を非対称に設ける場合は、例えば前記式(VI)で表されるハロゲン化アントラセン化合物において、ハロゲン原子 X¹ および X² のうち一方を、下記一般式(VII)

It can refine product with according to need recrystallization or column chromatography .

In this case, N,N- dimethylformamide , N- methyl pyrrolidone , chlorobenzene , dichlorobenzene , toluene , ethylacetate , chloroform , methylene chloride etc is ideal as refining solvent .

【0031】

It is good replacing N- substituent X of N- succinimide in according to need , aforementioned literature , to another halogen atom .

You can list reaction (Chemistry Letters (0366 - 7022, CMLTAG), 411 (1985)) which substitutes for example bromine atom in iodine atom .

Consequently, halogen compound which is acquired below-mentioned General Formulas (IV) and (V)

【0032】

[Chemical Formula 14]

【0033】

[Chemical Formula 15]

【0034】

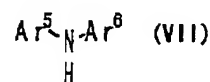
anthracene compound which is displayed with aforementioned General Formula (II) byreacting with aromatic boron derivative and Suzuki coupling method (Chemical Reviews , Vol.95, 2457 (1995)) which are displayed with the(In Formula, as for Ar³ and Ar⁴ when in Formula (II),synonymy, R³~R⁶ shows hydroxy group or optionally substituted alkoxy group , R³ and the R⁴, R⁵ and R⁶ connecting, are good forming ring.), is obtained.

【0035】

In addition like general formula (III) when substituent of type which differsis provided in asymmetry , in halogenation anthracene compound which is displayed with the for example aforementioned Formula (VI), inside one side of halogen atom X¹ and X², below-mentioned General Formula (VII)

【0036】

【化 16】



【0037】

(式中、 Ar^5 および Ar^6 は前記式(III)におけると同義)で表される芳香族アミン誘導体と Ullmann 反応(Organic Synthesis, 1 巻, 544 頁)、或いは Pd 法(Tetrahedron Letters, vol.39, 2367 (1998))により置換し、他方のハロゲン原子を上記の鈴木カップリング法などにより Ar^7 に対応する芳香族環で置換すればよい。

なお、 $-\text{NAr}^5\text{Ar}^6$ を導入する前に $-\text{Ar}^7$ を導入してもよい。

また、原料とする前記一般式(VI)で表わされる化合物において、ハロゲン原子 X^1 および X^2 を異なる原子(例えば Br と I)とすることにより、反応性の差を利用して、より収率よく、非対称化合物を得ることができる。

本発明における一般式(I)で表される化合物の代表例を、下記の表-1 に示すが、本発明化合物はこれに限定されるものではない。

【0038】

【表 1】

below-mentioned General Formula (VII)

【0036】

[Chemical Formula 16]

【0037】

If it substitutes aromatic amine derivative and Ullmann reaction which are displayed with (In Formula, as for $\text{Ar}^{⁵}$ and $\text{Ar}^{⁶}$ when in the aforementioned Formula (III), synonymy) (Organic Synthesis, Vol.1, 544 page), or with Pd method (Tetrahedron (0040 - 4020, TETRAB) Letters, vol.39, 2367 (1998)) and it should have substituted halogen atom of other with aromatic ring which corresponds to $\text{Ar}^{⁷}$ with above-mentioned Suzuki coupling method etc.

Furthermore, before introducing $-\text{NAr}^{⁵}\text{Ar}^{⁶}$, it is possible to introduce $-\text{Ar}^{⁷}$.

In addition, atom which differs (for example Br and I) with by doing, making use of difference of reactivity in compound which is displayed with the aforementioned General Formula (VI) which is made starting material, halogen atom $\text{X}^{¹}$ and the $\text{X}^{²}$, yield it is better, can acquire asymmetry compound.

representative example of compound which is displayed with General Formula (I) in the this invention, is shown in below-mentioned Table 1, but the compound of this invention is not something which is limited in this.

【0038】

[Table 1]

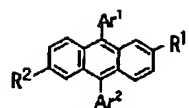


表-1

番号	Ar^1	Ar^2	R^1	R^2
(C-1)				
(C-2)				
(C-3)				
(C-4)				
(C-5)				
(C-6)				
(C-7)				
(C-8)				
(C-9)				
(C-10)				

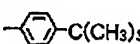
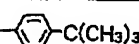


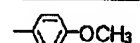
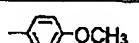














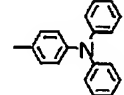
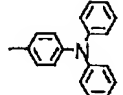






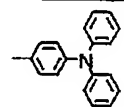



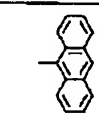



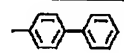



【0039】

【表 2】

[0039]

[Table 2]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-11)				
(C-12)				
(C-13)				
(C-14)				
(C-15)				
(C-16)				
(C-17)				
(C-18)				
(C-19)				
(C-20)				









































【0040】

【表 3】

[0040]

[Table 3]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-21)				
(C-22)				
(C-23)				
(C-24)				
(C-25)				
(C-26)				
(C-27)				
(C-28)				
(C-29)				
(C-30)				

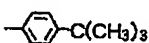
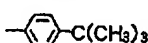


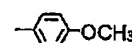
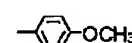














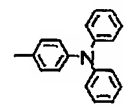
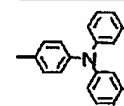






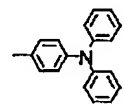



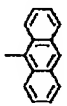



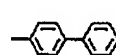



【0041】

【表 4】

[0041]

[Table 4]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-31)				
(C-32)				
(C-33)				
(C-34)				
(C-35)				
(C-36)				
(C-37)				
(C-38)				
(C-39)				
(C-40)				

































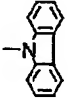
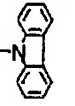






【0042】

【表 5】

[0042]

[Table 5]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-41)				
(C-42)				
(C-43)				
(C-44)				
(C-45)				
(C-46)				
(C-47)				
(C-48)				
(C-49)				
(C-50)				

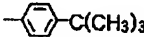
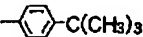


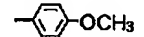
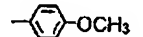














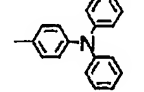
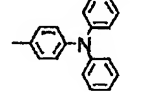






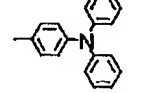







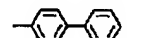



【0043】

【表 6】

[0043]

[Table 6]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-51)				
(C-52)				
(C-53)				
(C-54)				
(C-55)				
(C-56)				
(C-57)				
(C-58)				
(C-59)				
(C-60)				













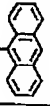
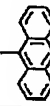


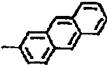
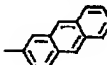


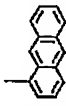
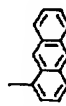










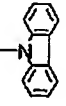







【0044】

[0044]

【表 7】

[Table 7]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-61)				
(C-62)				
(C-63)				
(C-64)				
(C-65)				
(C-66)				
(C-67)				
(C-68)				
(C-69)				
(C-70)				

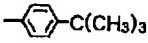
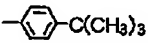
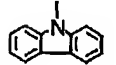
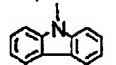
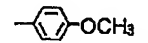
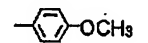
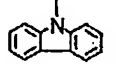
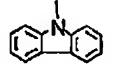

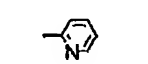
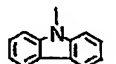
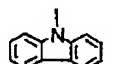

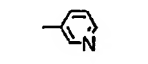
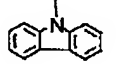
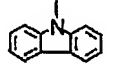
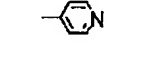
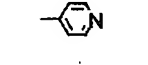
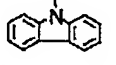
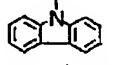
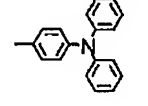
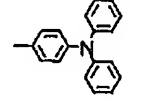
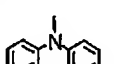
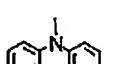
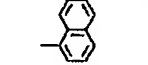
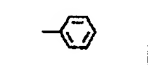
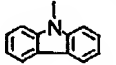
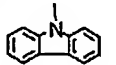
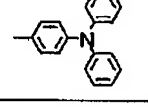
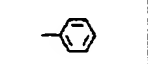
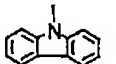
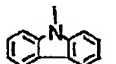
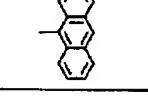
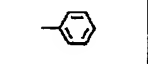
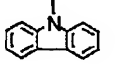
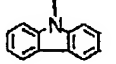
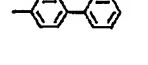
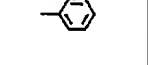
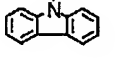
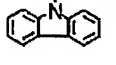
【0045】

【表 8】

[0045]

[Table 8]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-71)				
(C-72)				
(C-73)				
(C-74)				
(C-75)				
(C-76)				
(C-77)				
(C-78)				
(C-79)				
(C-80)				



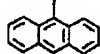
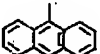


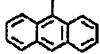
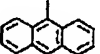


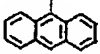
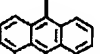


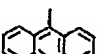
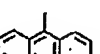


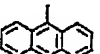
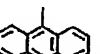


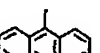
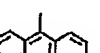


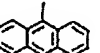
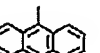


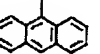
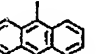


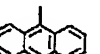
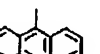


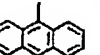
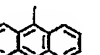
【0046】

[0046]

【表 9】

[Table 9]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-81)				
(C-82)				
(C-83)				
(C-84)				
(C-85)				
(C-86)				
(C-87)				
(C-88)				
(C-89)				
(C-90)				

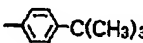
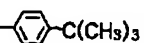


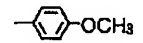
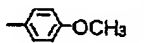


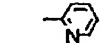
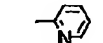


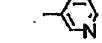
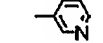


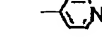
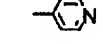


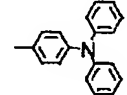
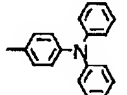


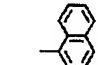
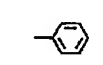


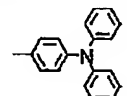
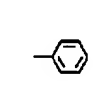


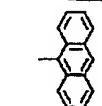
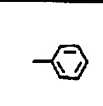


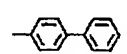
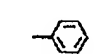


【0047】

【表 10】

[0047]

[Table 10]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-91)				
(C-92)				
(C-93)				
(C-94)				
(C-95)				
(C-96)				
(C-97)				
(C-98)				
(C-99)				
(C-100)				





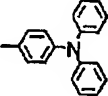







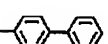





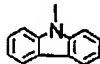

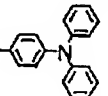

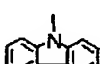



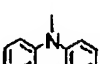

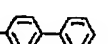

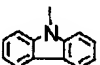

【0048】

[0048]

【表 11】

[Table 11]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-101)				
(C-102)				
(C-103)				
(C-104)				
(C-105)				
(C-106)				
(C-107)				
(C-108)				



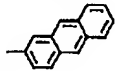
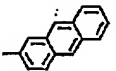


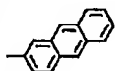
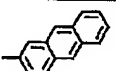


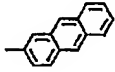
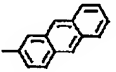
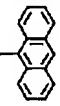
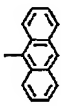
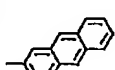
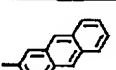
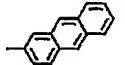
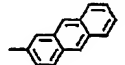
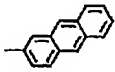
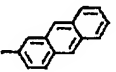
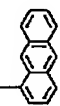
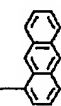
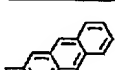
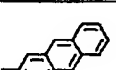


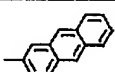
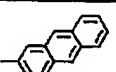
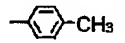
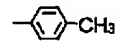
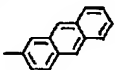
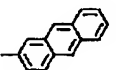


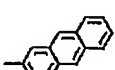
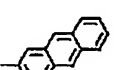


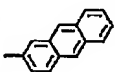
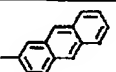
【0049】

【表 12】

[0049]

[Table 12]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-109)				
(C-110)				
(C-111)				
(C-112)				
(C-113)				
(C-114)				
(C-115)				
(C-116)				
(C-117)				
(C-118)				

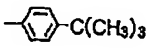
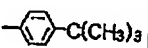
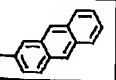
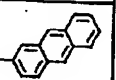
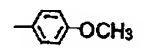
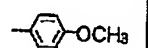
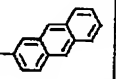
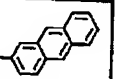


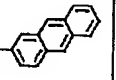
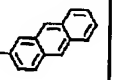


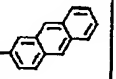
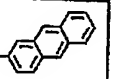
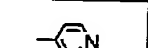
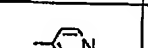
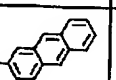
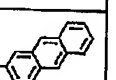
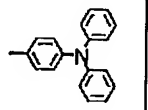
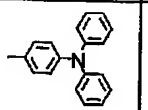
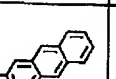
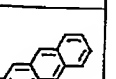
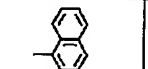
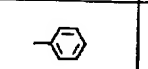
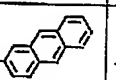
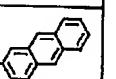
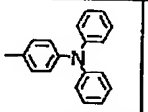
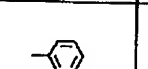
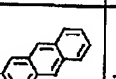
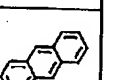
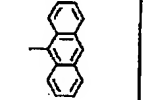
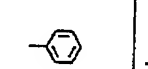
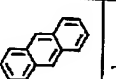
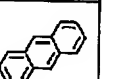
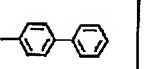
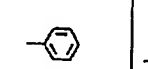
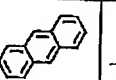
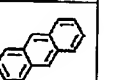
【0050】

[0050]

【表 13】

[Table 13]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-119)				
(C-120)				
(C-121)				
(C-122)				
(C-123)				
(C-124)				
(C-125)				
(C-126)				
(C-127)				
(C-128)				



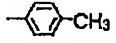
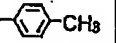





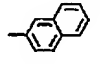
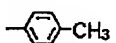
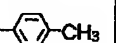
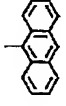
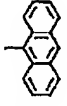


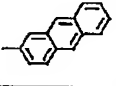
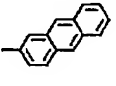
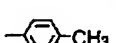

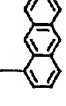
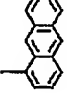
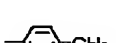



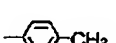

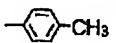
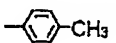
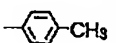
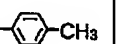
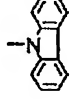
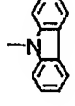
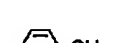



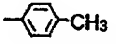
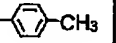
【0051】

【表 14】

[0051]

[Table 14]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-129)				
(C-130)				
(C-131)				
(C-132)				
(C-133)				
(C-134)				
(C-135)				
(C-136)				
(C-137)				
(C-138)				

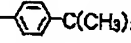
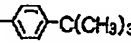
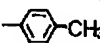

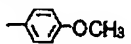
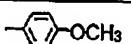
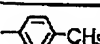



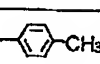

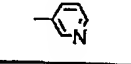
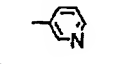
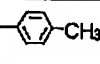

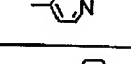
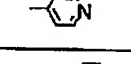
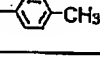

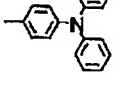
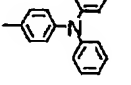
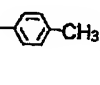

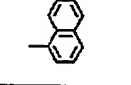
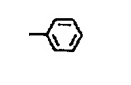
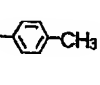

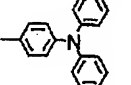
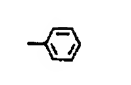
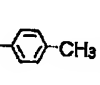

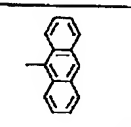
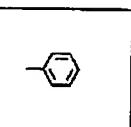
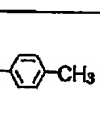
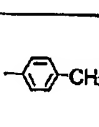
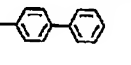
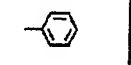
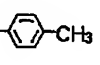

【0052】

[0052]

【表 15】

[Table 15]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-139)				
(C-140)				
(C-141)				
(C-142)				
(C-143)				
(C-144)				
(C-145)				
(C-146)				
(C-147)				
(C-148)				



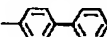







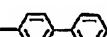





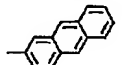
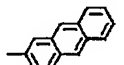










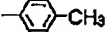
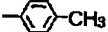
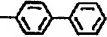
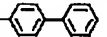






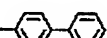

【0053】

【表 16】

[0053]

[Table 16]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-149)				
(C-150)				
(C-151)				
(C-152)				
(C-153)				
(C-154)				
(C-155)				
(C-156)				
(C-157)				
(C-158)				

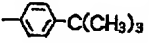
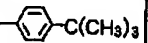
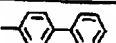
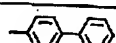
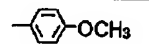
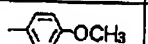


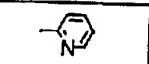
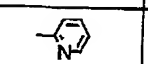
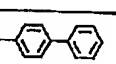
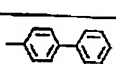
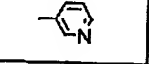
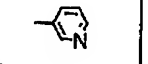
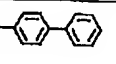
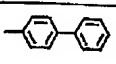
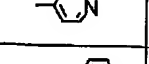
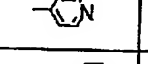
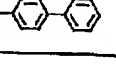
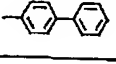
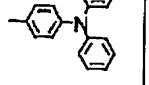
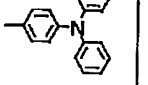
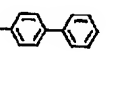
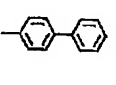
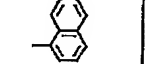
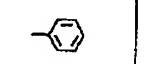
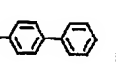
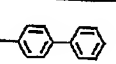
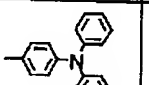
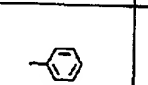
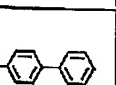
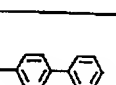
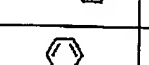


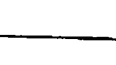
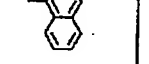

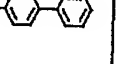
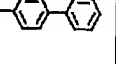
【0054】

【表 17】

[0054]

[Table 17]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-159)				
(C-160)				
(C-161)				
(C-162)				
(C-163)				
(C-164)				
(C-165)				
(C-166)				
(C-167)				
(C-168)				

















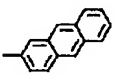
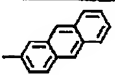










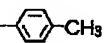
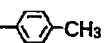


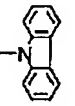
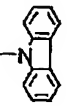






【0055】

【表 18】

[0055]

[Table 18]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-169)				
(C-170)				
(C-171)				
(C-172)				
(C-173)				
(C-174)				
(C-175)				
(C-176)				
(C-177)				
(C-178)				

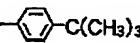
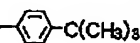


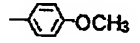
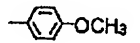














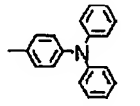
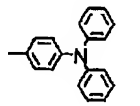






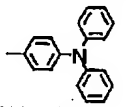



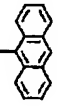



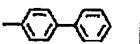



【0056】

【表 19】

[0056]

[Table 19]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-179)				
(C-180)				
(C-181)				
(C-182)				
(C-183)				
(C-184)				
(C-185)				
(C-186)				
(C-187)				
(C-188)				









































【0057】

【表 20】

[0057]

[Table 20]

【表-20】

番号	Ar ¹	Ar ²	Ar ⁷	Ar ⁸
(C-189)				
(C-190)				
(C-191)				
(C-192)				
(C-193)				
(C-194)				
(C-195)				
(C-196)				
(C-197)				
(C-198)				

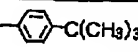
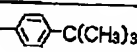


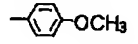
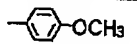














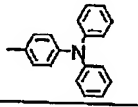
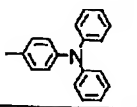






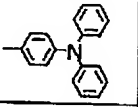







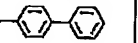





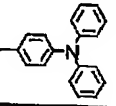
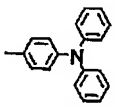


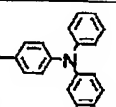
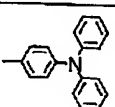
【0058】

【表 21】

[0058]

[Table 21]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-199)				
(C-200)				
(C-201)				
(C-202)				
(C-203)				
(C-204)				
(C-205)				
(C-206)				
(C-207)				
(C-208)				
(C-209)				
(C-210)				



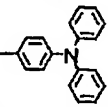
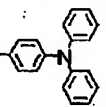


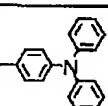
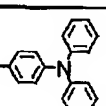


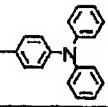
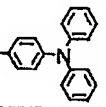


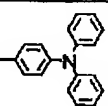
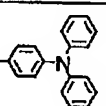


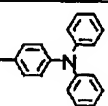
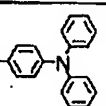


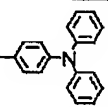
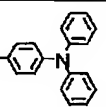


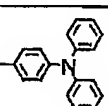
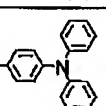


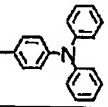
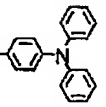


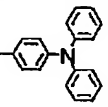
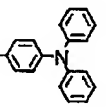
【0059】

【表 22】

[0059]

[Table 22]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-211)				
(C-212)				
(C-213)				
(C-214)				
(C-215)				
(C-216)				
(C-217)				
(C-218)				
(C-219)				

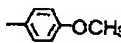
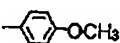
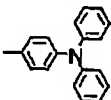
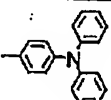


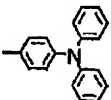
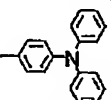


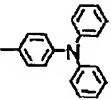
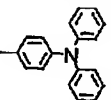


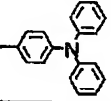
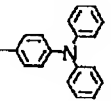
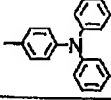
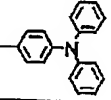
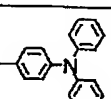
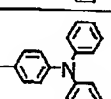


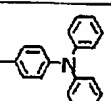
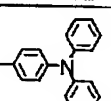
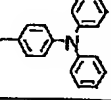

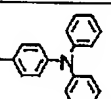
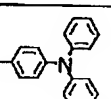


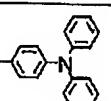
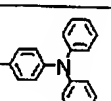
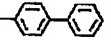

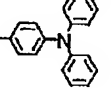
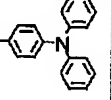
【0060】

[0060]

【表 23】

[Table 23]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-220)				
(C-221)				
(C-222)				
(C-223)				
(C-224)				
(C-225)				
(C-226)				
(C-227)				
(C-228)				



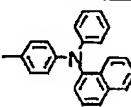
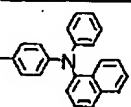


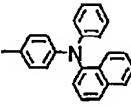
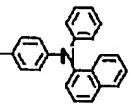


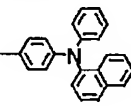
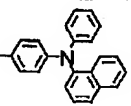
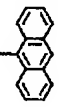
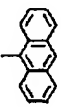
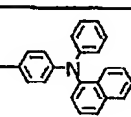
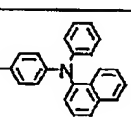


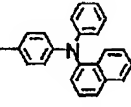
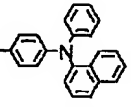


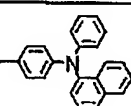
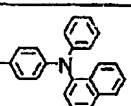


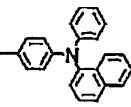
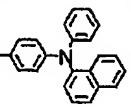


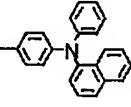
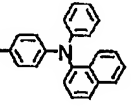
【0061】

【表 24】

[0061]

[Table 24]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-229)				
(C-230)				
(C-231)				
(C-232)				
(C-233)				
(C-234)				
(C-235)				
(C-236)				

【0062】

[0062]

【表 25】

[Table 25]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-237)				
(C-238)				
(C-239)				
(C-240)				
(C-241)				
(C-242)				
(C-243)				
(C-244)				



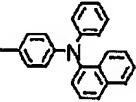
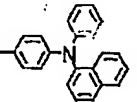
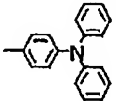

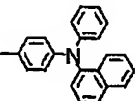
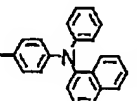
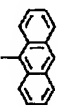

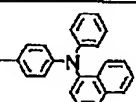
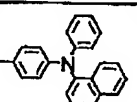
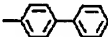

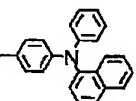
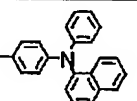


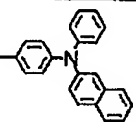
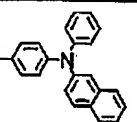


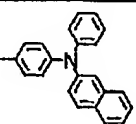
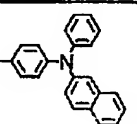


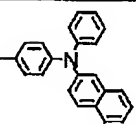
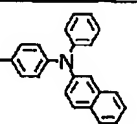
【0063】

【表 26】

[0063]

[Table 26]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-245)				
(C-246)				
(C-247)				
(C-248)				
(C-249)				
(C-250)				
(C-251)				

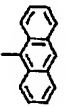
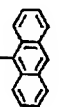
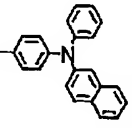
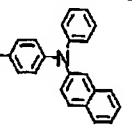
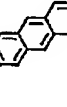
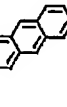
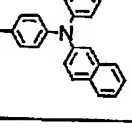
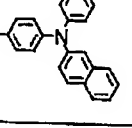
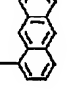
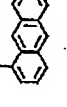
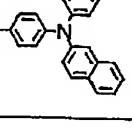
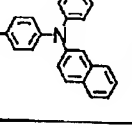
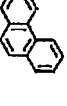
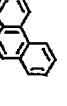
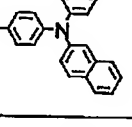
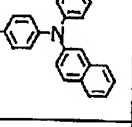


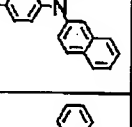
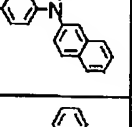
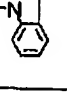
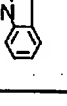
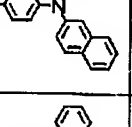
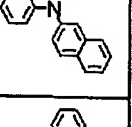
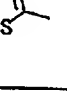
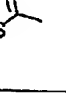
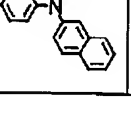
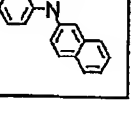
【0064】

[0064]

【表 27】

[Table 27]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-252)				
(C-253)				
(C-254)				
(C-255)				
(C-256)				
(C-257)				
(C-258)				

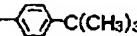
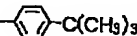
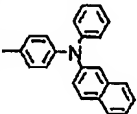
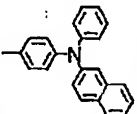
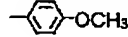
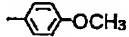
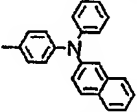
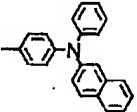


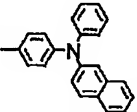
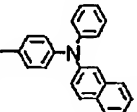


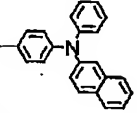
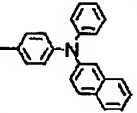


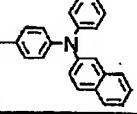
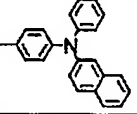
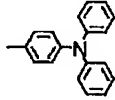
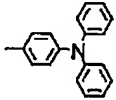
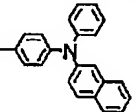
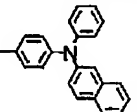


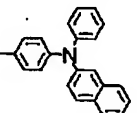
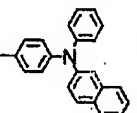
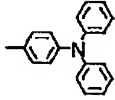

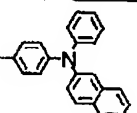
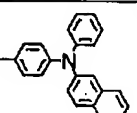
【0065】

【表 28】

[0065]

[Table 28]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-259)				
(C-260)				
(C-281)				
(C-262)				
(C-263)				
(C-264)				
(C-265)				
(C-266)				

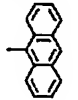

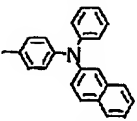
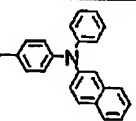
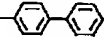

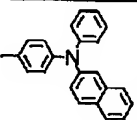
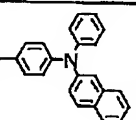


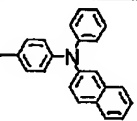
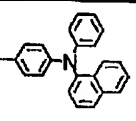


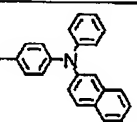
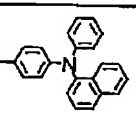

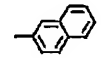
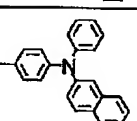
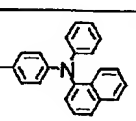
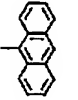
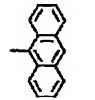
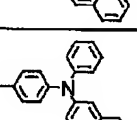
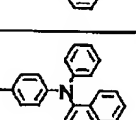
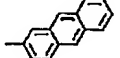
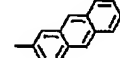
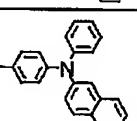
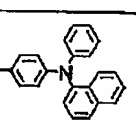
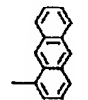
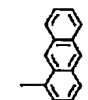
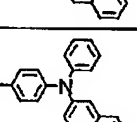
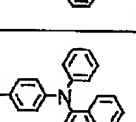
【0066】

[0066]

【表 29】

[Table 29]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-267)				
(C-268)				
(C-269)				
(C-270)				
(C-271)				
(C-272)				
(C-273)				
(C-274)				

【0067】

【表 30】

[0067]

[Table 30]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-275)				
(C-276)				
(C-277)				
(C-278)				
(C-279)				
(C-280)				
(C-281)				
(C-282)				



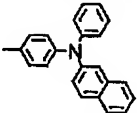
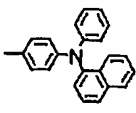
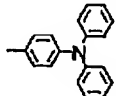
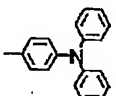
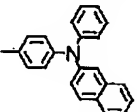
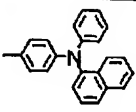


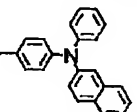
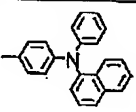
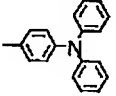

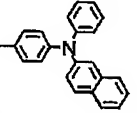
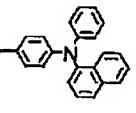


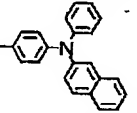
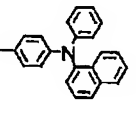
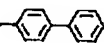

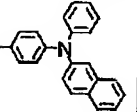
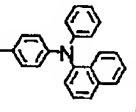



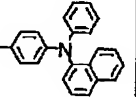



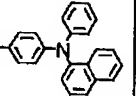
【0068】

【表 31】

[0068]

[Table 31]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-283)				
(C-284)				
(C-285)				
(C-286)				
(C-287)				
(C-288)				
(C-289)				
(C-290)				




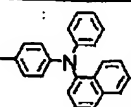



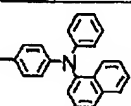
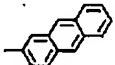
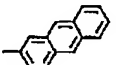

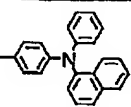



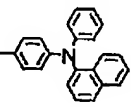



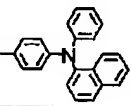
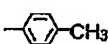
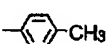

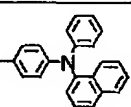



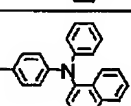



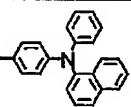
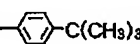
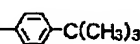

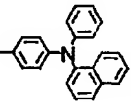
【0069】

【表 32】

[0069]

[Table 32]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-291)				
(C-292)				
(C-293)				
(C-294)				
(C-295)				
(C-296)				
(C-297)				
(C-298)				
(C-299)				

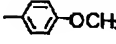
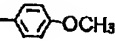

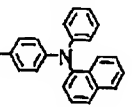



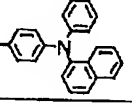



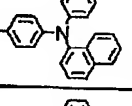



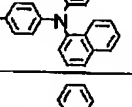
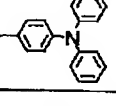
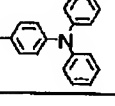

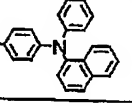



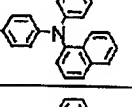
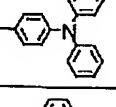


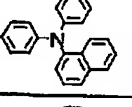



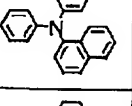
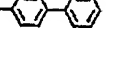


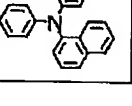
【0070】

【表 33】

[0070]

[Table 33]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-300)				
(C-301)				
(C-302)				
(C-303)				
(C-304)				
(C-305)				
(C-306)				
(C-307)				
(C-308)				



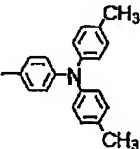
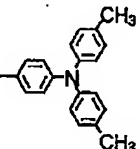


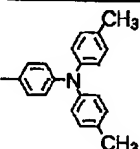
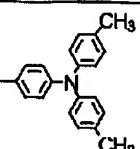
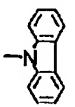
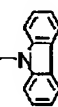
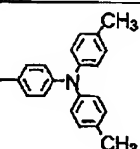
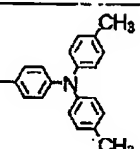


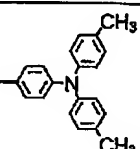
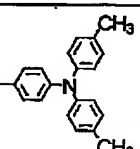
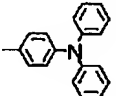
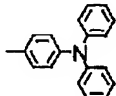
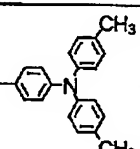
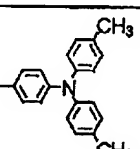


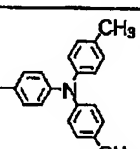
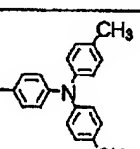
【0071】

【表 34】

[0071]

[Table 34]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-309)				
(C-310)				
(C-311)				
(C-312)				
(C-313)				
(C-314)				



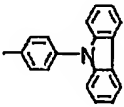
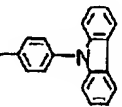


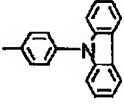
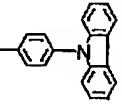


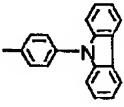
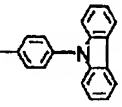


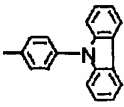
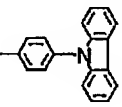
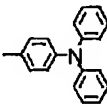
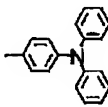
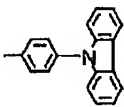
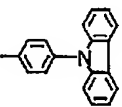


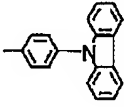
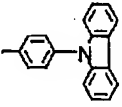
【0072】

[0072]

【表 35】

[Table 35]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-315)				
(C-316)				
(C-317)				
(C-318)				
(C-319)				
(C-320)				



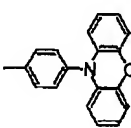
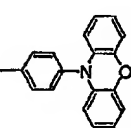


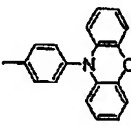
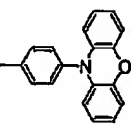
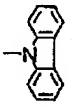
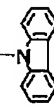
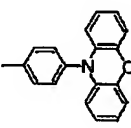
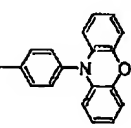


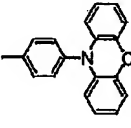
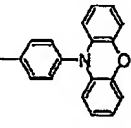
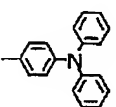
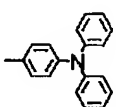
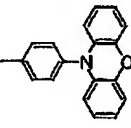
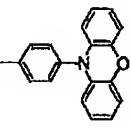


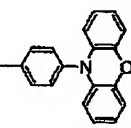
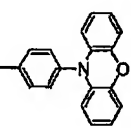
【0073】

【表 36】

[0073]

[Table 36]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-321)				
(C-322)				
(C-323)				
(C-324)				
(C-325)				
(C-326)				



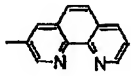
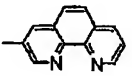


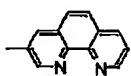
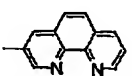


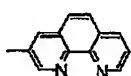
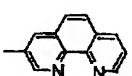


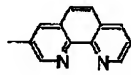
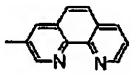
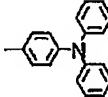
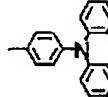
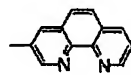
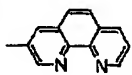


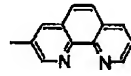
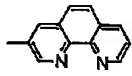
【0074】

[0074]

【表 37】

[Table 37]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-327)				
(C-328)				
(C-329)				
(C-330)				
(C-331)				
(C-332)				

【0075】

【表 38】

[0075]

[Table 38]

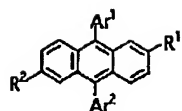


表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-1)				
(R-2)				
(R-3)				
(R-4)				
(R-5)				
(R-6)				
(R-7)				

【0076】

[0076]

【表 39】

[Table 39]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-8)				
(R-9)				
(R-10)				
(R-11)				
(R-12)				
(R-13)				
(R-14)				



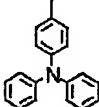

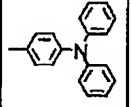
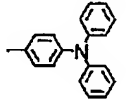
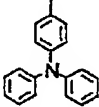



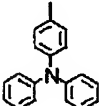

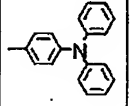

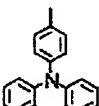

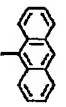

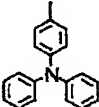

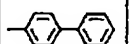

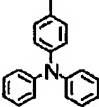




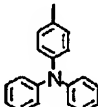
【0077】

[0077]

【表 40】

[Table 40]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-15)				
(R-16)				
(R-17)				
(R-18)				
(R-19)				
(R-20)				
(R-21)				

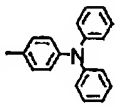


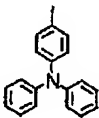



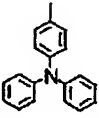
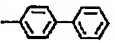


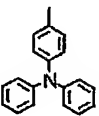


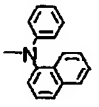
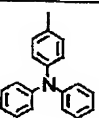


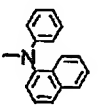
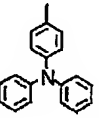
【0078】

[0078]

【表 41】

[Table 41]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-22)				
(R-23)				
(R-24)				
(R-25)				
(R-26)				





























【0079】

[0079]

【表 42】

[Table 42]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-27)				
(R-28)				
(R-29)				
(R-30)				
(R-31)				
(R-32)				
(R-33)				



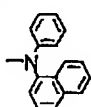
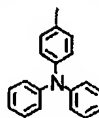
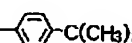
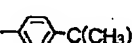
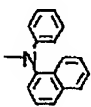
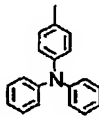
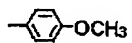
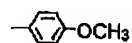
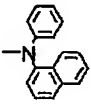
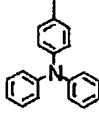


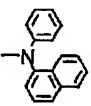
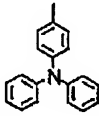


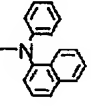
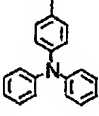


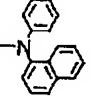
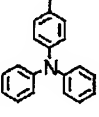
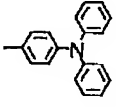
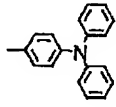
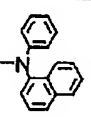
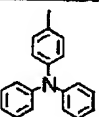
【0080】

[0080]

【表 43】

[Table 43]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-34)				
(R-35)				
(R-36)				
(R-37)				
(R-38)				
(R-39)				
(R-40)				



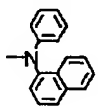
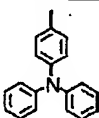
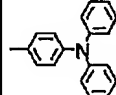

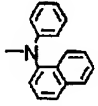
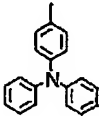


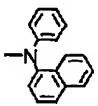
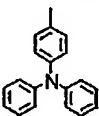
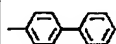

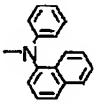
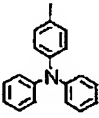


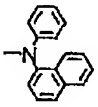
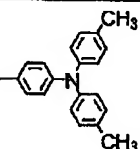


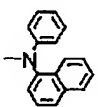
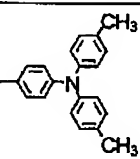


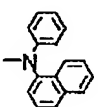
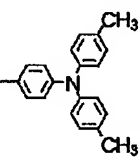
【0081】

[0081]

【表 44】

[Table 44]

表-1 (つづき)

符号	Ar-1	Ar-2	R ¹	R ²
(R-41)				
(R-42)				
(R-43)				
(R-44)				
(R-45)				
(R-46)				
(R-47)				

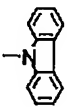
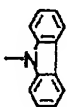
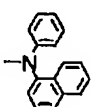
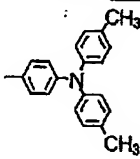
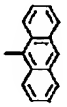
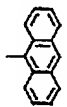
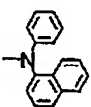
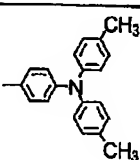


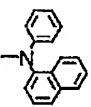
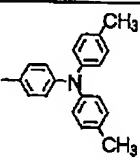
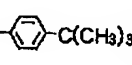
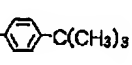
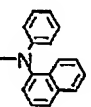
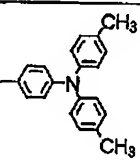
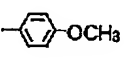
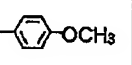
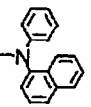
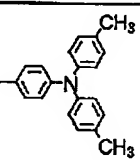


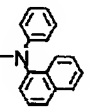
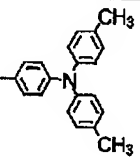
【0082】

[0082]

【表 45】

[Table 45]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-48)				
(R-49)				
(R-50)				
(R-51)				
(R-52)				
(R-53)				



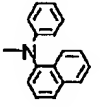
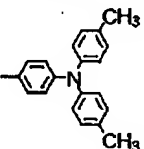


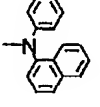
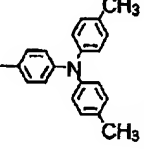
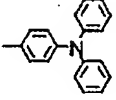
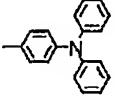
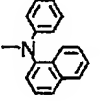
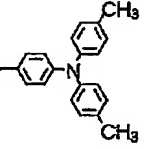


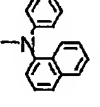
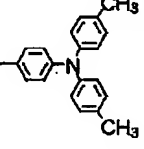
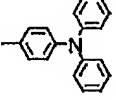

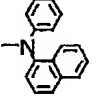
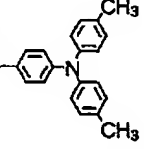
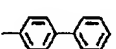

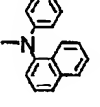
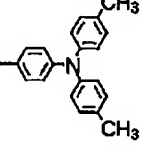
【0083】

【表 46】

[0083]

[Table 46]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-54)				
(R-55)				
(R-56)				
(R-57)				
(R-58)				
(R-59)				

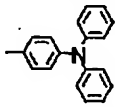
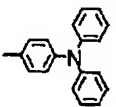
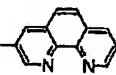

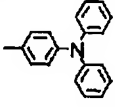

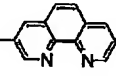



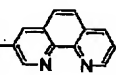
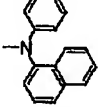


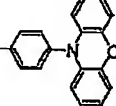
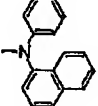


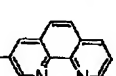
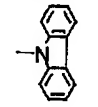


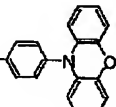
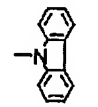
【0084】

【表 47】

[0084]

[Table 47]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-60)				
(R-61)				
(R-62)				
(R-63)				
(R-64)				
(R-65)				

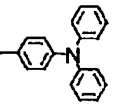
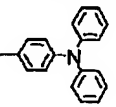
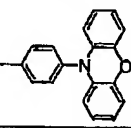
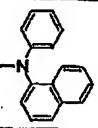
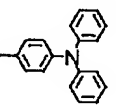
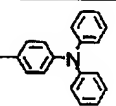
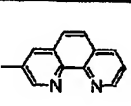
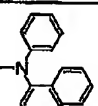
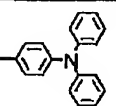
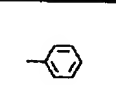
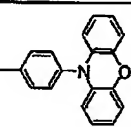
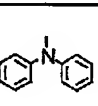
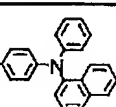
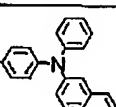
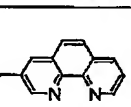
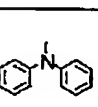
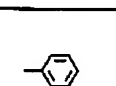
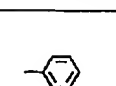
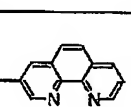
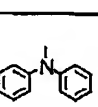
【0085】

【表 48】

[0085]

[Table 48]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-66)				
(R-67)				
(R-68)				
(R-69)				
(R-70)				



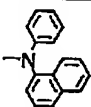
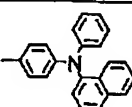


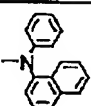
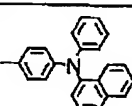


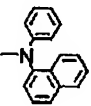
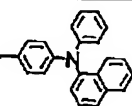
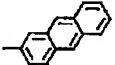
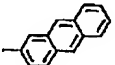
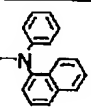
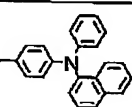
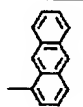
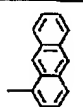
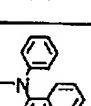
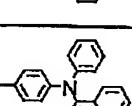

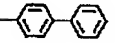
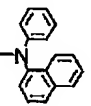
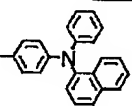
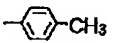
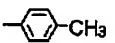
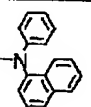
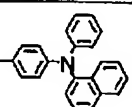
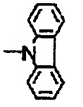
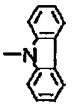
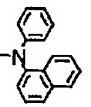
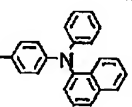
【0086】

【表 49】

[0086]

[Table 49]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-71)				
(R-72)				
(R-73)				
(R-74)				
(R-75)				
(R-76)				
(R-77)				
(R-78)				

【0087】

【表 50】

[0087]

[Table 50]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-79)				
(R-80)				
(R-81)				
(R-82)				
(R-83)				
(R-84)				
(R-85)				
(R-86)				
(R-87)				



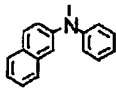
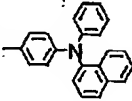


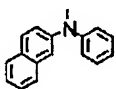
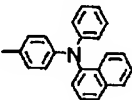


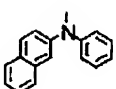
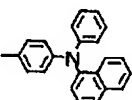


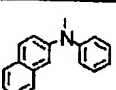
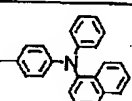


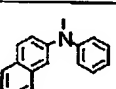
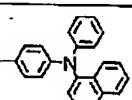


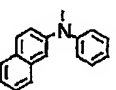
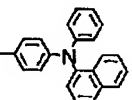


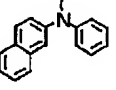
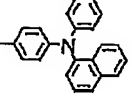


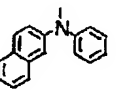
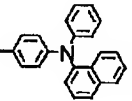
【0088】

【表 51】

[0088]

[Table 51]

表-1 (つづき)

符号	Ar ¹	Ar ²	R ¹	R ²
(R-88)				
(R-89)				
(R-90)				
(R-91)				
(R-92)				
(R-93)				
(R-94)				
(R-95)				

【0089】

【表 52】

[0089]

[Table 52]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-96)				
(R-97)				
(R-98)				
(R-99)				
(R-100)				
(R-101)				
(R-102)				
(R-103)				

【0090】

[0090]

【表 53】

[Table 53]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-104)				
(R-105)				
(R-106)				
(R-107)				
(R-108)				
(R-109)				
(R-110)				
(R-111)				

【0091】

【表 54】

[0091]

[Table 54]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-112)				
(R-113)				
(R-114)				
(R-115)				
(R-116)				
(R-117)				
(R-118)				
(R-119)				

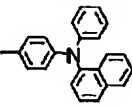
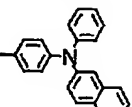
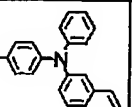
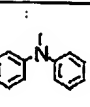


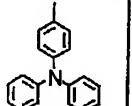



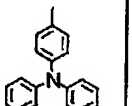

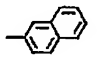

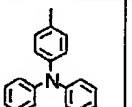

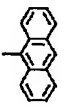
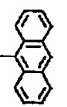
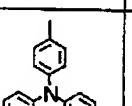

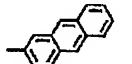
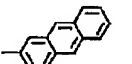
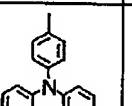

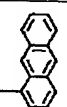
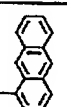
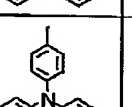

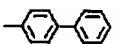
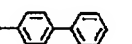
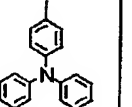

【0092】

[0092]

【表 55】

[Table 55]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-120)				
(R-121)				
(R-122)				
(R-123)				
(R-124)				
(R-125)				
(R-126)				
(R-127)				

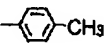
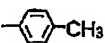
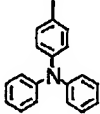

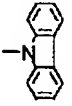
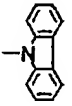
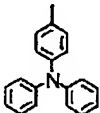



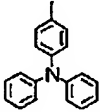

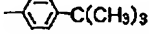

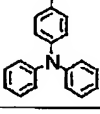

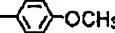
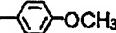
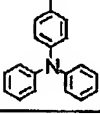



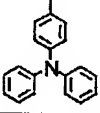



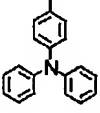



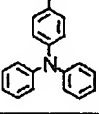

【0093】

【表 56】

[0093]

[Table 56]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-128)				
(R-129)				
(R-130)				
(R-131)				
(R-132)				
(R-133)				
(R-134)				
(R-135)				

【0094】

【表 57】

[0094]

[Table 57]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-136)				
(R-137)				
(R-138)				
(R-139)				
(R-140)				
(R-141)				
(R-142)				
(R-143)				

【0095】

【表 58】

[0095]

[Table 58]

表-1 (つづき)

符号	Ar ¹	Ar ²	R ¹	R ²
(R-144)				
(R-145)				
(R-146)				
(R-147)				
(R-148)				
(R-149)				
(R-150)				
(R-151)				

【0096】

[0096]

【表 59】

[Table 59]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(R-152)				
(R-153)				
(R-154)				
(R-155)				
(R-156)				

【0097】

次に、添付図面を参照して、本発明の有機電界発光素子の実施の形態を詳細に説明する。

図 1 は本発明に用いられる有機電界発光素子の構造の一例を模式的に示す断面図であるが、これに限定されるものではない。

1 は基板、2 は陽極、4 は正孔輸送層、5 は発光層、7 は陰極を各々表わす。

【0098】

基板 1 は有機電界発光素子の支持体となるものであり、石英やガラスの板、金属板や金属箔、プラスチックフィルムやシートなどが用いられる。

特にガラス板や、ポリエステル、ポリメタクリレート、ポリカーボネート、ポリスルホンなどの透明な合成樹脂の板が好ましい。

合成樹脂基板を使用する場合にはガスバリア性に留意する必要がある。

基板のガスバリア性が小さすぎると、基板を通過した外気により有機電界発光素子が劣化することがあるので好ましくない。

【0097】

Next, referring to attached figure, you explain embodiment of organic electroluminescent element of this invention in detail.

As for Figure 1 it is a sectional view which shows one example of structure of organic electroluminescent element which is used for this invention in schematic, but it is not something which is limited in this.

As for 1 as for substrate, 2 as for anode, 4 as for hole transporting layer, 5 light emitting layer, 7 cathode each you display.

【0098】

As for substrate 1 being something which becomes support of organic electroluminescent element, it can use sheet, metal plate and metal foil, plastic films and sheet etc of quartz and glass.

Especially glass sheet and sheet of polyester, polymethacrylate, polycarbonate, polysulfone or other transparent synthetic resin are desirable.

When synthetic resin substrate is used, it is necessary to consider to gas barrier property.

When gas barrier property of substrate is too small, because organic electroluminescent element deteriorates has, with external air which passes substrate it is not desirable.

このため、合成樹脂基板の少なくとも片面に緻密なシリコン酸化膜等を設けてガスバリア性を確保する方法も好ましい方法の一つである。

【0099】

基板 1 上には陽極 2 が設けられるが、陽極 2 は正孔輸送層への正孔注入の役割を果たすものである。

この陽極は、通常、アルミニウム、金、銀、ニッケル、パラジウム、白金等の金属、インジウム及び/またはスズの酸化物などの金属酸化物、ヨウ化銅などのハロゲン化金属、カーボンブラック、あるいは、ポリ(3-メチルチオフェン)、ポリピロール、ポリアニリン等の導電性高分子などにより構成される。

陽極 2 の形成は通常、スパッタリング法、真空蒸着法などにより行われることが多い。

また、銀などの金属微粒子、ヨウ化銅などの微粒子、カーボンブラック、導電性の金属酸化物微粒子、導電性高分子微粉末などの場合には、適当なバインダー樹脂溶液に分散し、基板 1 上に塗布することにより陽極 2 を形成することもできる。

さらに、導電性高分子の場合は電解重合により直接基板 1 上に薄膜を形成したり、基板 1 上に導電性高分子を塗布して陽極 2 を形成することもできる (Appl. Phys. Lett., 60 巻, 2711 頁, 1992 年)。

陽極 2 は異なる物質で積層して形成することも可能である。

陽極 2 の厚みは、必要とする透明性により異なる。

透明性が必要とされる場合は、可視光の透過率を、通常、60%以上、好ましくは 80%以上とすることが望ましく、この場合、厚みは、通常、5~1000nm、好ましくは 10~500nm 程度である。

不透明でよい場合は陽極 2 は基板 1 と同一でもよい。

また、さらには上記の陽極 2 の上に異なる導電材料を積層することも可能である。

【0100】

陽極 2 の上には正孔輸送層 4 が設けられる。

図 1 に示す構成の素子の場合、本発明の特徴である一般式(I)で表される化合物を含む層は、この正孔輸送層 4 として設けられる。

Because of this, synthetic resin substrate providing dense silicon oxide film etc at least in the one surface, also method which guarantees gas barrier property is one of the preferred method.

[0099]

It can provide anode 2 on substrate 1, but anode 2 is something which carries out role of positive hole injection to positive hole transport layer.

This anode configuration is done usually, oxide or other metal oxide, copper iodide or other metal halide, carbon black, or poly of the aluminum, gold, silver, nickel, palladium, platinum or other metal, indium and/or tin (3-methyl thiophene), by polypyrrole, polyaniline or other conductive polymer etc.

Formation of anode 2 usually is done by sputtering method, vacuum vapor deposition method etc is many.

In addition, in case of metal oxide fine particle, conductive polymer fine powder or other of silver or other metal fine particle, copper iodide or other fine particle, carbon black, electrical conductivity, it disperses to the suitable binder resin solution, it is possible also to form anode 2 by application doing on the substrate 1.

Furthermore, in case of conductive polymer directly it forms thin film, the application doing conductive polymer on substrate 1, it is possible also on substrate 1 to form anode 2, with electrolytic polymerization (Applied Physics Letters, Vol.60, 2711 page, 1992).

anode 2 laminating with substance which differs, forming is possible.

thickness of anode 2 differs depending upon transparency which is needed.

When transparency is needed, transmittance of visible light, as usually, is designated 60% or more, preferably 80% or more, it is desirable, in this case, the thickness, usually, is 5 - 1000 nm, preferably 10~500nm extent.

When it is possible to be a opaque, anode 2 may be same as the substrate 1.

In addition, furthermore also it is possible to laminate electrically conductive material which differs on above-mentioned anode 2.

[0100]

It can provide positive hole transport layer 4 on anode 2.

In case of element of configuration which is shown in Figure 1, the layer which includes compound which is displayed with General Formula (I) which is a feature of this invention is

この正孔輸送層 4 として設けられる。

なお、一般式(I)で表される化合物を含む層は、陽極と後述する発光層との間に存在すればよく、該層と陽極の間、または該層と発光層との間に任意の層を有していてもよい。

【0101】

一般に正孔輸送層の材料に要求される条件としては、陽極からの正孔注入効率が高く、かつ、注入された正孔を効率よく輸送することができる材料であることが必要である。

そのためには、イオン化ポテンシャルが小さく、可視光の光に対して透明性が高く、しかも正孔移動度が大きく、さらに安定性に優れ、トラップとなる不純物が製造時や使用時に発生しにくいことが要求される。

また、発光層 5 に接するために発光層からの発光を消光したり、発光層との間でエキサイプレックスを形成して効率を低下させないことが求められる。

上記の一般的要求以外に、車載表示用の応用を考えた場合、素子にはさらに耐熱性が要求される。

従って、T_gとして 85 deg C 以上の値を有する材料が望ましい。

【0102】

一般式(I)で表される化合物は、上記条件の多くを満たすため好ましい。

なお、正孔輸送層 4 は一般式(I)で表される化合物に加えて、公知の正孔輸送材料を含有していても良い。

正孔輸送層 4 は塗布法または真空蒸着法などで形成することができる。

塗布法の場合は、一般式(I)で表される化合物を少なくとも 1 種以上と、必要により正孔のトラップにならないバインダー樹脂や塗布性改良剤などの添加剤、とを添加し、溶解して塗布溶液を調製し、スピンコート法などの方法により陽極 2 上に塗布し、乾燥して正孔輸送層 4 を形成する。

バインダー樹脂としては、ポリカーボネート、ポリアリレート、ポリエステル等が挙げられる。

provided as this positive hole transport layer 4.

Furthermore, if layer which includes compound which is displayed with General Formula (I) anode between light emitting layer which it mentions later should have existed, is possible to have possessed layer of the option between between, or said layer and light emitting layer said layer and the anode .

【0101】

It is a material which can transport positive hole where positive hole injection efficiency from the anode was high as condition which is required to material of the positive hole transport layer generally, at same time, was filled efficiently, it is necessary .

For that, ionization potential is small, transparency is high vis-a-vis light of visible light , furthermore degree of positive hole transport is large, furthermore it is superior in stability , impurity which becomes trap is difficult to occur when producing and when using, it is required .

In addition, quenching doing light emitting from light emitting layer in order to touch to light emitting layer 5, forming [ekisaipurekkusu] between light emitting layer it does not decrease it can seek efficiency .

Other than above-mentioned general requiring, when of application of vehicle mounting display application was thought, furthermore heat resistance is required to element .

Therefore, as T_g, material which possesses value of 85 deg C or greater is desirable.

【0102】

compound which is displayed with General Formula (I), in order to fill up many of above-mentioned condition , is desirable.

Furthermore, hole transporting layer 4 is good containing positive hole transporting material of public knowledge in addition to compound which is displayed with General Formula (I).

It can form positive hole transport layer 4 with painting method or vacuum vapor deposition method etc.

In case of painting method , to add binder resin and paint improver or other additive , which do not become trap of positive hole , depending upon at least 1 kind and necessity melt and manufacture applied solution , application it does compound which is displayed with General Formula (I) on anode 2 with spin coating method or other method , dries and forms positive hole transport layer 4.

As binder resin , you can list polycarbonate , polyarylate , polyester etc.

バインダー樹脂は添加量が多いと正孔移動度を低下させるので、少ない方が望ましく、通常、50重量%以下が好ましい。

[0103]

真空蒸着法の場合には、一般式(I)で表される化合物を真空容器内に設置されたルツボに入れ、真空容器内を適当な真空ポンプで 10^{-4} Pa 程度にまで排気した後、ルツボを加熱して該化合物を蒸発させ、ルツボと向かい合って置かれた、陽極が形成された基板 1 上に正孔輸送層 4 を形成させる。

正孔輸送層 4 の膜厚は、通常、5~300nm、好ましくは 10~100nm である。

この様に薄い膜を様に形成するためには、一般に真空蒸着法がよく用いられる。

[0104]

正孔輸送層 4 の上には発光層 5 が設けられる。

発光層 5 は、電界を与えられた電極間において、陽極から注入されて正孔輸送層を移動する正孔と、陰極から注入されて電子輸送層 6 を移動する電子との再結合により励起されて強い発光を示す蛍光性化合物より形成される。

発光層 5 に用いられる蛍光性化合物としては、安定な薄膜形状を有し、固体状態で高い蛍光収率を示し、正孔および/または電子を効率よく輸送することができる化合物であることが必要である。

さらに電気化学的かつ化学的に安定であり、トラップとなる不純物が製造時や使用時に発生しにくい化合物であることが要求される。

[0105]

このような条件を満たす材料としては、8-ヒドロキシキノリンのアルミニウム錯体などの金属錯体(特開昭 59-194393 号公報)、10-ヒドロキシベンゾ[h]キノリンの金属錯体(特開平 6-322362 号公報)、ビススチリルベンゼン誘導体(特開平 1-245087 号公報、同 2-222484 号公報)、ビススチリルアリーレン誘導体(特開平 2-247278 号公報)、(2-ヒドロキシフェニル)ベンゾチアゾールの金属錯体(特開平 8-315983 号公報)、シロール誘導体等が挙げられる。

Because binder resin decreases when addition quantity is many, degree of positive hole transport, less one is desirable, usually, 50 weight % or less are desirable.

[0103]

In case of vacuum vapor deposition method, inserting compound which is displayed with the General Formula (I) in crucible which is installed inside vacuum vessel, inside the vacuum vessel with suitable vacuum pump exhaust after doing, heating crucible to 10^{-4} Pa extent and said compound evaporating, to face crucible, positive hole transport layer 4 is formed on substrate 1 where anode was formed.

membrane thickness of positive hole transport layer 4, usually, is 5 - 300 nm, preferably 10~100nm.

This way in order to form thin film evenly, it can use vacuum vapor deposition method generally well.

[0104]

It can provide light emitting layer 5 on positive hole transport layer 4.

As for light emitting layer 5, from anode being filled positive hole which moves positive hole transport layer and being filled from cathode in between electrode which can give electric field, excitation being done electron which moves the electron transport layer 6 by recombination, it is formed from fluorescence compound which shows strong light emitting.

It is a compound where stability it possesses thin film form condition as the fluorescence compound which is used for light emitting layer 5, shows high fluorescence yield with the solid state, can transport positive hole and/or electron efficiently, it is necessary.

Furthermore with electrochemical and chemically stable, impurity which becomes the trap is when producing and when using compound which is difficult to occur, it is required.

[0105]

8-hydroxy quinoline aluminum complex or other metal complex (Japan Unexamined Patent Publication Showa 59-194393 disclosure), 10-hydroxy benzo metal complex of [h] quinoline (Japan Unexamined Patent Publication Hei 6-322362 disclosure), the bisstyryl benzene derivative (Japan Unexamined Patent Publication Hei 1-245087 disclosure, same 2-222484 disclosure), bisstyryl arylene derivative (Japan Unexamined Patent Publication Hei 2-247278 disclosure), metal complex of (2-hydroxyphenyl) benzothiazole (Japan Unexamined Patent Publication Hei 8-315983 disclosure), you can list the [shirooru] derivative etc as material which fills up this kind of condition.

これらの発光層材料は、通常は真空蒸着法により正孔輸送層上に積層される。

[0106]

また、前述の正孔輸送層材料のうち、蛍光性を有する芳香族アミン系化合物も発光層材料として用いることができる。

発光層 5 の膜厚は、通常、3~200 nm、好ましくは 5~100 nm である。

発光層も正孔輸送層と同様の方法で形成することができるが、通常は真空蒸着法が用いられる。

[0107]

素子の発光効率を向上させるとともに発光色を変える目的で、例えば、8-ヒドロキシキノリンのアルミニウム錯体をホスト材料として、クマリン等のレーザー用蛍光色素をドーピングすること(J. Appl. Phys., 65 巻, 3610 頁, 1989 年)等が行われている。

このドーピング手法は、発光層 5 にも適用でき、ドーピング用材料としては、クマリン以外にも各種の蛍光色素が使用できる。

青色発光を与える蛍光色素としては、ペリレン、ピレン、アントラセン、クマリンおよびそれらの誘導体等が挙げられる。

緑色蛍光色素としては、キナクリドン誘導体、クマリン誘導体等が挙げられる。

黄色蛍光色素としては、ルブレン、ペリミドン誘導体等が挙げられる。

赤色蛍光色素としては、DCM 系化合物、ベンゾピラン誘導体、ローダミン誘導体、ベンゾチオキサテン誘導体、アザベンゾチオキサテン等が挙げられる。

[0108]

上記のドーピング用蛍光色素以外にも、ホスト材料に応じて、レーザー研究, 8 巻, 694 頁, 803 頁, 958 頁(1980 年); 同 9 巻, 85 頁(1981 年)、に列挙されている蛍光色素が発光層用のドーピング材料として使用することができる。

ホスト材料に対して上記蛍光色素がドーピングされる量は、 10^{-3} ~10 重量%が好ましい。

[0109]

上述の蛍光色素を発光層のホスト材料にドーピングする方法を以下に説明する。

These light emitting layer material usually are laminated on hole transporting layer by vacuum vapor deposition method .

[0106]

In addition, it uses among aforementioned positive hole transport layer material , aromatic amine type compound which possesses fluorescence as light emitting layer material it is possible .

membrane thickness of light emitting layer 5, usually, is 3 - 200 nm , preferably 5~100 nm .

It can form with method where also light emitting layer is similar to the positive hole transport layer , but usually it can use vacuum vapor deposition method .

[0107]

light emission efficiency of element as it improves, with objective which changes emission color , thing (Journal of Applied Physics (0021 - 8979, JAPIAU), 6 Vol.5 , 3610page , 1989) etc which fluorescent pigment for coumarin or other laser dope is done is done with aluminum complex of for example 8-hydroxy quinoline as host material .

Be able to apply this doping technique , to also light emitting layer 5, you can use various fluorescent pigment in addition to coumarin as material for dope .

You can list perylene , pyrene , anthracene , coumarin and those derivative etc as fluorescent pigment which gives blue light emitting .

As green color fluorescent pigment , you can list quinacridone derivative , coumarin derivative etc.

As yellow fluorescent pigment , you can list rubrene , [perimidon] derivative etc.

As red color fluorescent pigment , you can list DCM compound , benzopyran derivative , rhodamine derivative , benzo thioxanthene derivative , aza benzo thioxanthene etc.

[0108]

In addition to fluorescent pigment for above-mentioned dope according to host material , laser research and Vol.8 , 694page , 803page , 958page (1980); same Vol.9 , 85page (1981) , you can use fluorescent pigment which is enumerated as dopant charge for light emitting layer .

Above-mentioned fluorescent pigment as for quantity which dope is done, 10^{-3} ~10 weight % is desirable vis-a-vis host material .

[0109]

Above-mentioned fluorescent pigment method which dope is done is explained to host material of light emitting layer

する方法を以下に説明する。

塗布の場合は、前記発光層ホスト材料と、ドーブ用蛍光色素、さらに必要により、電子のトラップや発光の消光剤とならないバインダー樹脂や、レベリング剤等の塗布性改良剤などの添加剤を添加し溶解した塗布溶液を調整し、スピンコート法などの方法により正孔輸送層 4 上に塗布し、乾燥して発光層 5 を形成する。

バインダー樹脂としては、ポリカーボネート、ポリアリレート、ポリエステル等が挙げられる。

バインダー樹脂は添加量が多いと正孔/電子移動度を低下させるので、少ない方が望ましく、50重量%以下が好ましい。

[0110]

真空蒸着法の場合には、前記ホスト材料を真空容器内に設置されたるつぼに入れ、ドーブする蛍光色素を別のつぼに入れ、真空容器内を適当な真空ポンプで 10^{-6} Torr 程度にまで排気した後、各々のつぼを同時に加熱して蒸発させ、つぼと向かい合って置かれた基板上に層を形成する。

また、他の方法として、上記の材料を予め所定比で混合したものを同一のつぼを用いて蒸発させてもよい。

[0111]

上記各ドーパントが発光層中にドーブされる場合、発光層の膜厚方向において均一にドーブされるが、膜厚方向において濃度分布があっても構わない。

例えば、正孔輸送層側の界面近傍にのみドーブしたり、逆に、陰極側の界面近傍にドーブしてもよい。

陰極 7 は、発光層 5 に電子を注入する役割を果たす。

陰極 7 として用いられる材料は、前記陽極 2 に使用される材料を用いることが可能であるが、効率よく電子注入を行なうには、仕事関数の低い金属が好ましく、スズ、マグネシウム、インジウム、カルシウム、アルミニウム、銀等の適当な金属またはそれらの合金が用いられる。

具体例としては、マグネシウム-銀合金、マグネシウム-インジウム合金、アルミニウム-リチウム合金等の低仕事関数合金電極が挙げられる。

さらに、陰極と発光層または電子輸送層の界面

below.

In case of application, it adds binder resin and leveling agent or other paint improver or other additive which do not become trap of electron and quenching agent of light emitting and the aforementioned light emitting layer host material and fluorescent pigment, for dope furthermore in accordance with necessary, it adjusts applied solution which is melted, the application it does on positive hole transport layer 4 with spin coating method or other method, dries and forms light emitting layer 5.

As binder resin, you can list polycarbonate, polyarylate, polyester etc.

Because binder resin decreases when addition quantity is many, positive hole /electron mobility, less one is desirable, 50 weight % or less are desirable.

[0110]

In case of vacuum vapor deposition method, inserting aforementioned host material in crucible which is installed inside vacuum vessel, fluorescent pigment which dope is done inserting in another crucible, inside vacuum vessel with suitable vacuum pump exhaust after doing, heating each crucible simultaneously to 10^{-6} Torr extent and evaporating, it forms layer on substrate to face crucible.

In addition, it is possible to evaporate those which mix the above-mentioned material beforehand at specified ratio as other method, making use of same crucible.

[0111]

When above-mentioned each dopant dope it is done in light emitting layer, dope it is done in uniform, in film thickness, direction of light emitting layer, but the concentration distribution may be in film thickness direction.

dope it does in only boundary vicinity of for example positive hole transport layer side, conversely, dope is possible to boundary vicinity of cathode side to do.

cathode 7 carries out role which fills electron to light emitting layer 5.

material which is used as cathode 7 uses material which is used for aforementioned anode 2, it is possible, but to do electron injection efficiently, metal where work function is low is desirable, tin, magnesium, indium, calcium, aluminum, silver or other suitable metal or can use those alloy.

As embodiment, you can list magnesium-silver alloy, magnesium-indium alloy, aluminum-lithium alloy or other low work function alloy electrode.

Furthermore, cathode and also fact that insert LiF, Mg

に LiF、MgF₂、Li₂O 等の極薄絶縁膜(0.1~5nm)を挿入することも、素子の効率を向上させる有効な方法である(Appl. Phys. Lett., 70 巻,152 頁,1997 年;特開平 10-74586 号公報;IEEE Trans.Electron. Devices,44 巻,1245 頁,1997 年)。

陰極 7 の膜厚は通常、陽極 2 と同様である。

低仕事関数金属から成る陰極を保護する目的で、この上にさらに、仕事関数が高く大気に対して安定な金属層を積層することは素子の安定性を増す。

この目的のために、アルミニウム、銀、銅、ニッケル、クロム、金、白金等の金属が使われる。

[0112]

正孔注入の効率をさらに向上させ、かつ、有機層全体の陽極への付着力を改善させる目的で、正孔輸送層 4 と陽極 2 との間に陽極バッファ層 3 を挿入することも行われている(図 2 参照)。

陽極バッファ層 3 を挿入することで、初期の素子の駆動電圧が下がると同時に、素子を定電流で連続駆動した時の電圧上昇も抑制される効果がある。

陽極バッファ層に用いられる材料に要求される条件としては、陽極とのコンタクトがよく均一な薄膜が形成でき、熱的に安定、すなわち、融点及びガラス転移温度が高く、融点としては 300 deg C 以上、ガラス転移温度としては 100 deg C 以上が要求される。

さらに、イオン化ポテンシャルが低く陽極からの正孔注入が容易なこと、正孔移動度が大きいことが挙げられる。

[0113]

この目的のために、これまでに銅フタロシアニン等のフタロシアニン化合物(特開昭 63-295695 号公報)、ポリアニリン(Appl. Phys. Lett., 64 巻, 1245 頁,1994 年)、ポリチオフェン(Optical Materials, 9 巻, 125 頁, 1998 年)等の有機化合物や、スパッタ・カーボン膜(Synth. Met., 91 巻, 73 頁, 1997 年)や、バナジウム酸化物、ルテニウム酸化物、モリブデン酸化物等の金属酸化物(J. Phys.D, 29 巻, 2750 頁, 1996 年)が報告されている。

[0114]

For other extremely thin insulating film (0.1 - 5 nm) the light emitting layer or electron transport layer in boundary, efficiency of element is effective method which improves, (Applied Physics Letters, 70 volume, 152 page, 1997; Japan Unexamined Patent Publication Hei 10-74586 disclosure; IEEE Trans. electron. devices, Vol.44, 1245 page, 1997).

membrane thickness of cathode 7 usually is similar to anode 2.

With objective which protects cathode which consists of low work function metal, furthermore, work function stability laminating metal layer increases the stability of element on this vis-a-vis atmosphere highly.

Because of this objective, aluminum, silver, copper, nickel, chromium, gold, platinum or other metal is used.

[0112]

Efficiency of positive hole injection furthermore improving, at same time, with objective which improves adhesion force to anode of organic layer entirety, also the positive hole transport layer 4 and inserting anode buffer layer 3 between anode 2 are done, (Figure 2 reference).

When by fact that anode buffer layer 3 is inserted, drive voltage of element of initial stage goes down when simultaneously, continuous drive doing element with constant current, there is an effect to which also voltage increase is controlled.

contact of anode be able to form uniform thin film well as condition which is required to material which is used for anode buffer layer, stability, namely, melting point and glass transition temperature are high in thermal, 100 deg C or greater are required as 300 deg C or greater, glass transition temperature as melting point.

Furthermore, ionization potential to be low positive hole injection from anode is easy, the degree of positive hole transport is large, it is listed.

[0113]

Because of this objective, copper phthalocyanine or other phthalocyanine compound (Japan Unexamined Patent Publication Showa 63- 295695 disclosure), polyaniline (Applied Physics Letters, Vol.64, 1245 page, 1994), polythiophene (optical Materials, Vol.9, 125 page, 1998) or other organic compound and sputter * carbon film (Synth. Met., 9 Vol.1, 73 page, 1997) and, vanadium oxide, ruthenium oxide, molybdenum oxide or other metal oxide (J. Phys.D, Vol.29, 2750 page, 1996) is reported so far.

[0114]

陽極バッファ層の場合も、正孔輸送層と同様にして薄膜形成可能であるが、無機物の場合には、さらに、スパッタ法や電子ビーム蒸着法、プラズマ CVD 法が用いられる。

以上の様にして形成される陽極バッファ層 3 の膜厚は、通常、3~100nm、好ましくは 5~50nm である。

【0115】

素子の発光効率をさらに向上させることを目的として、発光層 5 と陰極 7 の間に電子輸送層 6 を設けてもよい。

電子輸送層 6 は、電界を与えられた電極間において陰極から注入された電子を効率よく発光層 5 の方向に輸送することができる化合物より形成される。

電子輸送層 6 に用いられる電子輸送性化合物としては、陰極 7 からの電子注入効率が高く、かつ、高い電子移動度を有し注入された電子を効率よく輸送することができる化合物であることが必要である。

【0116】

このような条件を満たす材料としては、8-ヒドロキシキノリンのアルミニウム錯体などの金属錯体(特開昭 59-194393 号公報)、10-ヒドロキシベンゾ[h]キノリンの金属錯体、オキサジアゾール誘導体、ジスチリルビフェニル誘導体、シロール誘導体、3-または 5-ヒドロキシフラボン金属錯体、ベンゾオキサゾール金属錯体、ベンゾチアゾール金属錯体、トリスベンズイミダゾリルベンゼン(米国特許第 5,645,948 号)、キノキサリン化合物(特開平 6-207169 号公報)、フェナントロリン誘導体(特開平 5-331459 号公報)、2-t-ブチル-9,10-N,N'-ジシアノアントラキノンジイミン、n 型水素化非晶質炭化シリコン、n 型硫化亜鉛、n 型セレン化亜鉛などが挙げられる。

電子輸送層 6 の膜厚は、通常、5~200nm、好ましくは 10~100 nm である。

【0117】

電子輸送層 6 は、正孔輸送層 4 と同様にして塗布法あるいは真空蒸着法により発光層 5 上に積層することにより形成される。

通常は、真空蒸着法が用いられる。

尚、図 1 とは逆の構造、すなわち、基板上に陰極 7、発光層 5、正孔輸送層 4、陽極 2 の順に積層することも可能であり、既述したように少なくとも

Also case of anode buffer layer, it is thin film formation possible with as similar to positive hole transport layer, but in case of inorganic substance, furthermore, it can use the sputtering method and electron beam vapor deposition method, plasma CVD method.

membrane thickness of anode buffer layer 3 which is formed like above, usually, is 3 - 100 nm, preferably 5~50nm.

【0115】

Furthermore it improves light emission efficiency of element as objective, it is possible to provide electron transporting layer 6 between light emitting layer 5 and cathode 7.

As for electron transporting layer 6, it is formed from compound which can transport the electron which was filled from cathode in between electrode which can give electric field to direction of light emitting layer 5 efficiently.

It is a compound which can transport electron which possessed electron mobility where electron injection efficiency from cathode 7 is high as electron transport ability compound which is used for electron transport layer 6, at same time, is high was filled and efficiently, it is necessary.

【0116】

8-hydroxy quinoline aluminum complex or other metal complex (Japan Unexamined Patent Publication Showa 59-194393 disclosure), 10-hydroxy benzo metal complex, oxadiazole derivative, distyryl biphenyl derivative, [shirooru] derivative, 3-of [h] quinoline or 5-hydroxy flavone metal complex, benzoxazole metal complex, benzothiazole metal complex, tris benzimidazolyl benzene, (U. S. Patent No. 5,645,948 number), quinoxaline compound. (Japan Unexamined Patent Publication Hei 6-207169 disclosure), phenanthroline derivative (Japan Unexamined Patent Publication Hei 5-331 459 disclosure), you can list 2-t-butyl -9,10-N,N'-di cyano anthraquinone diimine, n-type hydrogenation amorphous silicon carbide, n-type zinc sulfide, n-type zinc selenide etc as material which fills up this kind of condition.

membrane thickness of electron transport layer 6, usually, is 5 - 200 nm, preferably 10~100 nm.

【0117】

electron transporting layer 6 is formed by laminating on light emitting layer 5 with painting method or the vacuum vapor deposition method to similar to hole transporting layer 4.

Usually, it can use vacuum vapor deposition method.

Furthermore also being possible on structure, namely, substrate of opposite to Figure 1 to laminate in order of cathode 7, light emitting layer 5, positive hole transport layer

も一方が透明性の高い 2 枚の基板の間に本発明の有機電界発光素子を設けることも可能である。

同様に、図 2 または図 3 に示した前記各層構成とは逆の構造に積層することも可能である。

【0118】

本発明は、有機電界発光素子が、単一の素子、アレイ状に配置された構造からなる素子、陽極と陰極が X-Y マトリックス状に配置された構造のいずれにおいても適用することができる。

【0119】

【実施例】

以下に実施例及び試験例を挙げて本発明を具体的に説明するが、本発明はその要旨を越えない限りこれらの例に限定されるものではない。

なお、以下の実施例における化合物の No. は表 -1 の化合物の No. に対応する。

合成例 1(2,6-ジブロモ-9,10-ジフェニルアントラセンの合成)

9,10-ジフェニルアントラセン 8.58g(26mmol)と、N-ブロモコハク酸イミド 23.13g(130mmol)を 177ml の N,N-ジメチルホルムアミドに加え、窒素下、80 deg C で 36.5 時間反応させた。

反応終了後、沈殿を濾別し、メタノール洗浄、アセトン洗浄を行い、5.18g の黄褐色粉末状の 2,6-ジブロモ-9,10-ジフェニルアントラセンを得た(収率 41%)。

質量分析値 MS=486 で目的物と一致した。

融点 310 deg C。

¹H-NMR により、臭素の置換位置が 2 位と 6 位であることを確認した。

【0120】

¹H-NMR(CDCl₃ (δ =ppm)):7.37(dd,2H), 7.42(m,4H), 7.53(d,2H), 7.58(m,2H), 7.61(m,4H), 7.82(d,2H)

【0121】

【化 17】

4, anode 2, as previously mentioned done, also it is possible to provide organic electroluminescent element of this invention between 2 substrate where at least one transparency is high.

In same way, also it is possible to laminate in structure of opposite to aforementioned each layer configuration which is shown in Figure 2 or Figure 3 .

【0118】

organic electroluminescent element , in which of structure where element , anode and cathode which consist of structure which is arranged in single element , array are arranged in X-Y matrix state it can apply this invention.

【0119】

[Working Example(s)]

Listing Working Example and Test Example below, you explain this invention concretely, but if the this invention does not exceed gist , it is not something which is limited as these examples.

Furthermore, No. of compound in Working Example below corresponds to No. of compound of Table 1 .

synthesis example 1 (2 and 6 -dibromo -9,10-biphenyl anthracene synthesis)

9 and 10 -biphenyl anthracene 8.58g (26 mmol) with, N-bromo succinimide 23.13g (130 mmol) in addition to N,N-dimethylformamide of 177 ml , under nitrogen , 36.5 hours it reacted with 80 deg C.

After reaction termination , precipitation was filtered, methanol wash , acetone washing was done, the yellow-brown powder of 5.18 g 2 and 6 -dibromo -9,10-biphenyl anthracene were acquired (yield 41%).

It agreed with object compound with mass analysis value MS =486.

melting point 310 deg C.

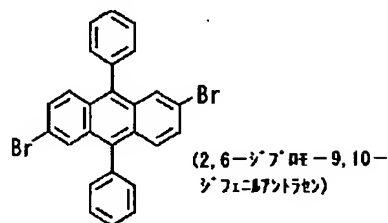
With ¹H-nmr , substituted position of bromine is 2 position and 6 position , you verified .

【0120】

¹H-nmr (CD Cl₃ (δ =ppm)): 7.37 (dd,2H) , 7.42 (m,4H) , 7.53 (d,2H) , 7.58 (m,2H) , 7.61 (m,4H) , 7.82 (d,2H)

【0121】

[Chemical Formula 17]



【0122】

合成例 2(2,6-ジヨード-9,10-ジフェニルアントラセンの合成)

合成例 1 で得られた 2,6-ジブロモ-9,10-ジフェニルアントラセン 4.98g(10mmol)と、ヨウ化カリウム 41.73g(251mmol)、ヨウ化銅 15.86g(83mmol)を 30ml のヘキサメチルリン酸トリアミドに加え、窒素下、145 deg C で 8 時間反応させた。

反応終了後、1 規定塩酸水溶液中に放出し、生じた沈殿を濾別、水洗した。

その後メタノール洗浄し、クロロホルムに可溶分のみ回収した。

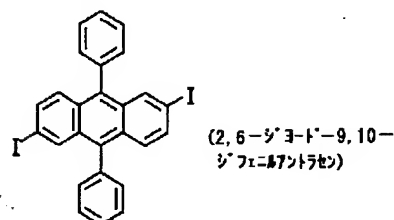
溶媒留去後、4.93g の黄色粉末状の 2,6-ジヨード-9,10-ジフェニルアントラセンを得た(収率 83%)。

MS=582 で目的物と一致した。

融点 301 deg C。

【0123】

【化 18】



【0124】

実施例 1(化合物 C-209 の合成)

合成例 1 で得られた 2,6-ジブロモ-9,10-ジフェニルアントラセン 0.82g(1.7mmol)と、下記芳香族ホウ素誘導体(B-1)

【0125】

【化 19】

【0122】

synthesis example 2 (2 and 6 -di iodo -9,10-biphenyl anthracene synthesis)

Under nitrogen , 8 -hour it reacted with 145 deg C 2 and 6 itacquires with synthesis example 1 - [jiburomoo] 9 and 10 -biphenyl anthracene 4.98g (10 mmol) with, potassium iodide 41.73g (251 mmol),copper iodide 15.86g (83 mmol) in addition to hexamethyl phosphoric acid triamide of 30 ml .

It discharged after reaction termination , and in 1 normal hydrochloric acid solution it filtered theprecipitation which it occurs, water wash did.

After that methanol wash it did, only soluble fraction recovered in chloroform .

After solvent removal , yellow powder of 4.93 g 2 and 6 -di iodo -9,10-biphenyl anthracene were acquired(yield 83%) .

It agreed with object compound with MS =582.

melting point 301 deg C.

【0123】

【Chemical Formula 18】

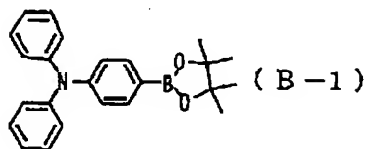
【0124】

Working Example 1 (Synthesis of compound C-209)

2 and 6 -dibromo -9,10-biphenyl anthracene 0.82g where it acquires with synthesis example 1 (1.7 mmol) with, thebelow-mentioned aromatic boron derivative (B-1)

【0125】

【Chemical Formula 19】



【0126】

1.32g(3.6mmol)、リン酸三カリウム 1.50g(7.1mmol)、テトラキス(トリフェニルフォスフィノ)パジウム 0.09g(0.08mmol)を 12ml の乾燥 N,N-ジメチルホルムアミドに加え、窒素下、100 deg C で 6 時間反応させた。

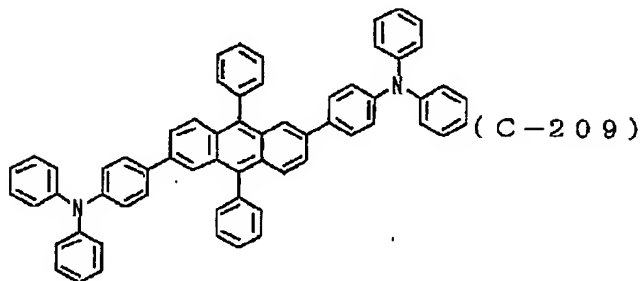
反応終了後、生成した沈殿を濾別し、水洗浄、熱アセトン懸洗し、1.18g の黄色粉末状の 2,6-ビス {4-(N,N-ジフェニルアミノ)フェニル}-9,10-ジフェニルアントラセンを得た(収率 86%)。

MS=816 で目的物と一致した。

またセイコー電子社製 DSC-20 により示差熱分析測定したところ、ガラス転移温度(Tg)は 171 deg C、融点 440 deg C と大変高い値を示した。

【0127】

【化 20】



【0128】

次に、ガラス基板をアセトンで超音波洗浄、純水で水洗、イソプロピルアルコールで超音波洗浄、乾燥窒素で乾燥、UV/オゾン洗浄を行った後、真空蒸着装置内に設置して、装置内の真空度が 3×10^{-6} Torr 以下になるまで油拡散ポンプを用いて排気した。

化合物(C-209)をセラミックるつぽに入れ、るつぽの周囲のタンタル線ヒーターで加熱して蒸着を行った。

蒸着時の真空度は 7.0×10^{-7} Torr(約 9.3×10^{-5} Pa)で、蒸着速度 0.1nm/秒で膜厚 98nm の一様で

【0126】

1.32 g (3.6 mmol), tripotassium phosphate 1.50g (7.1 mmol), tetrakis (triphenyl phosphino) palladium 0.09g (0.08 mmol) in addition to drying N,N- dimethylformamide of 12 ml, under nitrogen, 6 -hour reaction it did with 100 deg C.

After reaction termination, it filtered precipitation which is formed, water washing, hot acetone Kake washing did, yellow powder of 1.18 g 2 and 6 -bis {4 - (N,N- diphenylamino) phenyl } - acquired 9 and 10 -biphenyl anthracene (yield 86%).

It agreed with object compound with MS =816.

In addition with Seiko Instruments Inc. (DB 69-058-2077) supplied DSC-20 when differential thermal analysis it does, glass transition temperature (Tg) 171 deg C, melting point 440 deg C showed very much high value.

【0127】

[Chemical Formula 20]

【0128】

Next, glass substrate with acetone with ultrasonic cleaning, pure water with water wash, isopropyl alcohol is dried with ultrasonic cleaning, dry nitrogen, after washing UV/ozone, until it installed inside the vacuum vapor deposition equipment, degree of vacuum inside equipment 3×10^{-6} Torr or less ago, exhaust it did making use of oil scattering pump.

You inserted compound (C-209) in ceramic crucible, heated with tantalum line heater of periphery of crucible and did vapor deposition.

degree of vacuum at time of vapor deposition with 7.0×10^{-7} Torr (Approximately 9.3

透明な膜を得た。

この薄膜試料のイオン化ポテンシャルを理研計器(株)製の紫外線電子分析装置(AC-1)を用いて測定したところ、5.27eV の値を示した。

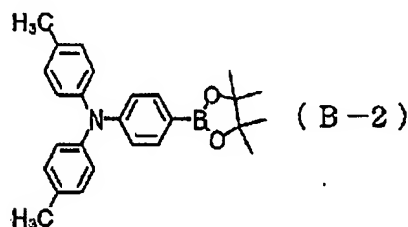
また、この薄膜試料の蛍光を測定したところ、励起波長 363nm で 486、536nm の発光ピークを示した。

実施例 2(化合物 C-309 の合成)

(B-1)の代わりに下記芳香族ホウ素誘導体(B-2)

【0129】

【化 21】



【0130】

を用いた以外は実施例 1 と同様に合成し、1.32g の橙色粉末状の 2,6-ビス{4-(N,N-ジ(p-トリル)アミノ)フェニル}-9,10-ジフェニルアントラセンを得た(収率 79%)。

MS=872 で目的物と一致した。

またセイコー電子社製 DSC-20 により示差熱分析測定したところ、ガラス転移温度(Tg)は 162 deg C と大変高い値を示した。

融点 353 deg C。

【0131】

【化 22】

x10⁻⁵Pa), membrane thickness 98nm being even with vapor deposition rate 0.1 nm/sec , acquired transparent film .

When ionization potential of this thin film specimen was measured Riken Keiki Co. Ltd. (DB 69-057-3670) make making use of ultraviolet light electron analyzer (AC-1), value of 5.27 eV was shown.

In addition, when fluorescence of this thin film specimen was measured, light emitting peak of 486,536 nm was shown with excitation wavelength 363nm .

Working Example 2 (Synthesis of compound C-309)

In place of (B-1) below-mentioned aromatic boron derivative (B-2)

[0129]

[Chemical Formula 21]

[0130]

Other than using, it synthesized in same way as Working Example 1, the amber powder of 1.32 g 2 and 6 -bis { 4 - (N,N- di (p- tolyl) amino) phenyl } - acquired 9 and 10 -biphenyl anthracene (yield 79%).

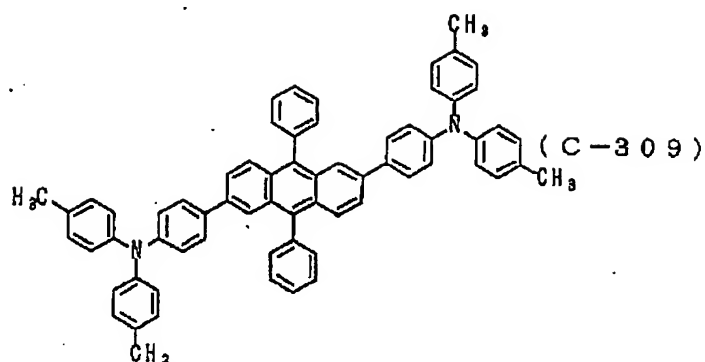
It agreed with object compound with MS =872.

In addition with Seiko Instruments Inc. (DB 69-058-2077) supplied DSC-20 when differential thermal analysis it does, glass transition temperature (Tg) 162 deg C showed very much high value.

melting point 353 deg C.

[0131]

[Chemical Formula 22]



【0132】

化合物(C-209)と同様に、化合物(C-309)をセラミックるつぽに入れ、ガラス基板上に膜厚 78nm の一様で透明な膜を得た。

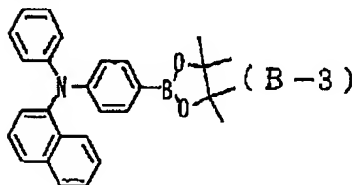
この薄膜試料のイオン化ポテンシャルを測定したところ 5.05eV の値を示した。

実施例 3(化合物 C-229 の合成)

(B-1)の代わりに下記芳香族ホウ素誘導体(B-3)

【0133】

【化 23】



【0134】

を用いた以外は実施例 1 と同様に合成し、0.54g の黄色粉末状の 2,6-ビス{4-(N-(1-ナフチル)-N-フェニルアミノ)フェニル}-9,10-ジフェニルアントラセンを得た(収率 55%)。

MS=916 で目的物と一致した。

またセイコー電子社製 DSC-20 により示差熱分析測定したところ、ガラス転移温度(Tg)は 170 deg C、融点 436 deg C と大変高い値を示した。

【0135】

【化 24】

【0132】

compound (C-209) with in same way, compound (C-309) was inserted in the ceramic crucible , membrane thickness 78nm it was even on glass substrate and transparent film was acquired.

When ionization potential of this thin film specimen was measured value of 5.05 eV was shown.

Working Example 3 (Synthesis of compound C-229)

In place of (B-1) below-mentioned aromatic boron derivative (B-3)

【0133】

[Chemical Formula 23]

【0134】

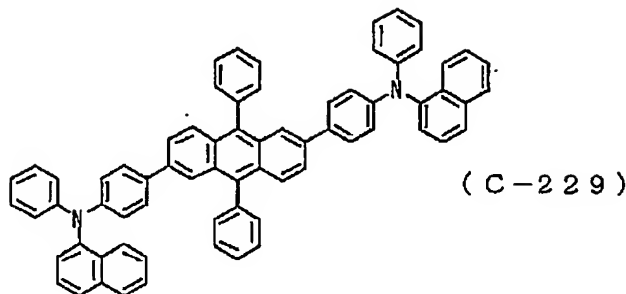
Other than using, it synthesized in same way as Working Example 1, the yellow powder of 0.54 g 2 and 6 -bis {4 - (N- (1 -naphthyl) -N- phenylamino) phenyl } - acquired 9 and 10 -biphenyl anthracene (yield 55%).

It agreed with object compound with MS =916.

In addition with Seiko Instruments Inc. (DB 69-058-2077) supplied DSC-20 when differential thermal analysis it does, glass transition temperature (Tg) 170 deg C, melting point 436 deg C showed very much high value.

【0135】

[Chemical Formula 24]



【0136】

化合物(C-209)と同様に、化合物(C-229)をセラミックのつぼに入れ、ガラス基板上に膜厚 84nm の一様で透明な膜を得た。

この薄膜試料のイオン化ポテンシャルを測定したところ 5.31eV の値を示した。

実施例 4(化合物 R-71 の合成)

合成例 2 にて得られた 2,6-ジヨード-9,10-ジフェニルアントラセン 3.1g(5.3mmol)と、ジフェニルアミン 1.2g(5.3mmol)、炭酸カリウム 1.7g(12.3mmol)、銅粉 1.1g(16.7mmol)を 20ml のテトラエチレングリコールジメチルエーテルに加え、窒素下、180 deg C で 11 時間反応させた。

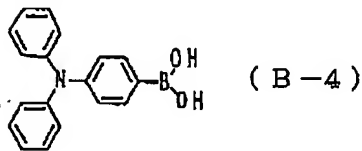
反応終了後、メタノールを添加、濾液を回収した。

その後、シリカゲルを用いたカラムクロマトグラフィーにより精製し、0.94g の 2-(N-(1-ナフチル)-N-フェニル)アミノ-6-ブロモ-9,10-ジフェニルアントラセンを得た(収率 26%)。

得られた 2-ヨード-6-(N-(1-ナフチル)-N-フェニル)アミノ-9,10-ジフェニルアントラセン 0.94g(1.4mmol)、下記芳香族ホウ素誘導体 (B-4)0.66g(1.9mmol)、

【0137】

【化 25】



【0138】

テトラキス(トリフェニルフォスフィノ)パラジウム 0.03g(0.03mmol)を 10ml のトルエンと 3ml の 2

【0136】

compound (C-209) with in same way, compound (C-229) was inserted in the ceramic crucible , membrane thickness 84nm it was even on glass substrate and transparent film was acquired.

When ionization potential of this thin film specimen was measured value of 5.31 eV was shown.

Working Example 4 (Synthesis of compound R-71)

Under nitrogen , 11 hour it reacted with 180 deg C 2 and 6 -di iodo -9,10-biphenyl anthracene 3.1g where it acquires with synthesis example 2 (5.3 mmol) with, diphenylamine 1.2g (5.3 mmol) , potassium carbonate 1.7g (12.3 mmol) , copper powder 1.1g (16.7 mmol) in addition to tetraethylene glycol dimethyl ether of 20 ml .

After reaction termination , it added methanol , filtrate recovered.

After that, it refined with column chromatography which uses silica gel , acquired 2- (N- (1 -naphthyl) -N- phenyl) amino -6-bromo -9,10-biphenyl anthracene of 0.94 g (yield 26%) .

2 -iodo -6- where it acquires (N- (1 -naphthyl) -N- phenyl) amino -9,10-biphenyl anthracene 0.94g (1.4 mmol) , below-mentioned aromatic boron derivative (B-4) 0.66 g (1.9 mmol) ,

【0137】

【Chemical Formula 25】

【0138】

tetrakis (triphenyl phosphino) palladium 0.03g (0.03 mmol) in addition to toluene of 10 ml and the mixed solution of 2

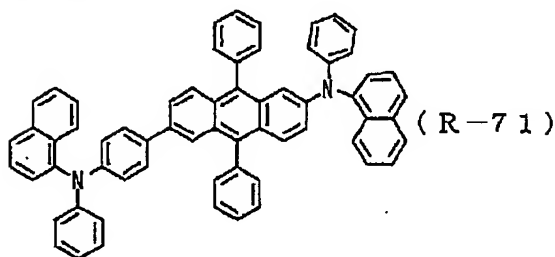
規定炭酸ナトリウム水溶液の混合溶液に加え、窒素下、90 deg C で 5 時間反応させた。

反応終了後、生成した沈殿を濾別し、トルエン可溶分を得た。

溶媒留去後、熱メタノール懸洗し、0.94g の黄土色粉末状の 2-(N-(1-ナフチル)-N-フェニル)アミノ-6-{4-(N-(1-ナフチル)-N-フェニルアミノ)フェニル}-9,10-ジフェニルアントラセンを得た(収率 80%)。

【0139】

【化 26】



【0140】

MS=840 で目的物と一致した。

またセイコー電子社製 DSC-20 により示差熱分析測定したところ、ガラス転移温度(Tg)は 158 deg C と大変高い値を示した。

化合物(C-229)から芳香族連結基の一つ抜いた非対称形だが、Tg はあまり下がらず、耐熱性が維持された。

化合物(C-209)と同様に、化合物(R-71)をセラミックるつぽに入れ、ガラス基板上に膜厚 67.5nm の一様で透明な膜を得た。

この薄膜試料のイオン化ポテンシャルを測定したところ 5.12eV の値を示した。

【0141】

実施例 5

図 3 に示す構造を有する有機電界発光素子を以下の方法で作製した。

ガラス基板 1 上にインジウム・スズ酸化物(ITO)透明導電膜を 120nm 堆積したもの(ジオマテック社製;電子ビーム成膜品;シート抵抗 15Ω)を通常のフォトリソグラフィ技術と塩酸エッチングを用いて 2mm 幅のストライプにパターンニングして陽極 2 を形成した。

normal sodium carbonate aqueous solution of 3 ml , under nitrogen , 5 hours it reacted with 90 deg C.

After reaction termination , precipitation which is formed was filtered, the toluene-soluble fraction was acquired.

After solvent removal , hot methanol wash it did, 2 - (N- (1 -naphthyl) -N- phenyl) amino -6- of the yellowish earthen color powder of 0.94 g { 4 - (N- (1 -naphthyl) -N- phenylamino) phenyl } - acquired 9 and 10 -biphenyl anthracene (yield 80%) .

【0139】

[Chemical Formula 26]

【0140】

It agreed with object compound with MS =840.

In addition with Seiko Instruments Inc. (DB 69-058-2077) supplied DSC-20 when differential thermal analysis it does, glass transition temperature (Tg) 158 deg C showed very much high value.

It is a asymmetric shape which aromatic connecting group one was pulled out from compound (C-229) , but Tg excessively did not go down, heat resistance was maintained.

compound (C-209) with in same way, compound (R-71) was inserted in the ceramic crucible , membrane thickness 67.5nm it was even on glass substrate and transparent film was acquired.

When ionization potential of this thin film specimen was measured value of 5.12 eV was shown.

【0141】

Working Example 5

organic electroluminescent element which possesses structure which is shown in Figure 3 was produced with method below.

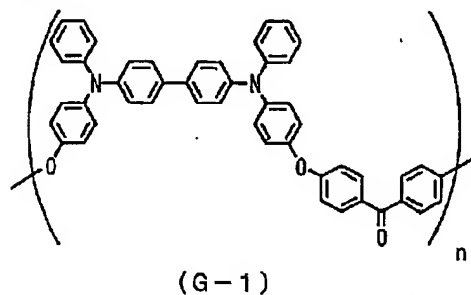
On glass substrate 1 patterning doing thing (Geomatec Co. Ltd. (DB 69-066-3968) supplied ;electron beam film formation item; sheet resistance 15Ω) which indium * tin oxide (ITO) transparent conductive film 120 nm is accumulated in stripe of 2 mm width making use of conventional photolithography technology and hydrochloric acid etching , it formed anode 2

パターン形成した ITO 基板をアセトンによる超音波洗浄、純水による水洗、イソプロピルアルコールによる超音波洗浄の順で洗浄後、窒素ブローで乾燥させ、最後に紫外線オゾン洗浄を行った。

次に陽極バッファ層 3 として芳香族ジアミン含有ポリエーテル(G-1);重量平均分子量 25000;ガラス転移温度 199 deg C)

[0142]

[化 27]

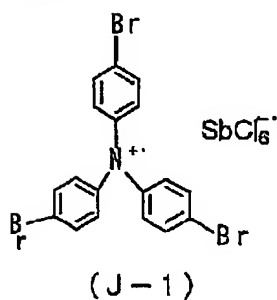


[0143]

及び、その 10 重量%のアクセプタ-(J-1)

[0144]

[化 28]



[0145]

を下記の条件で、上記ガラス基板上にスピコートした:

acid etching , it formed anode 2.

With acetone with ultrasonic cleaning , pure water with water wash , isopropyl alcohol in order of ultrasonic cleaning after washing, drying ITO substrate which pattern formation is done with the nitrogen blowing , you washed lastly ultraviolet light ozone .

Next as anode buffer layer 3 aromatic diamine content polyether (G-1); weight average molecular weight 25000;glass transition temperature 199 deg C)

[0142]

[Chemical Formula 27]

[0143]

And, acceptor of 10 weight % (J-1)

[0144]

[Chemical Formula 28]

[0145]

With below-mentioned condition , spin coating it did on theabove-mentioned glass substrate :

溶媒	1, 2-ジクロロエタン		
solvent	1 and 2 -dichloroethane		
塗布液濃度	30[mg/ml]		

coating solution concentration	30 [mg/ml]		
スピナ回転数	2500[rpm]		
spinner rotation rate	2500 [rpm]		
スピナ回転時間	25[秒]		
spinner rotation time	25 [second]		
乾燥条件	90 分間自然乾燥		
drying condition	90 min natural drying		

【0146】

上記のスピコートにより 30nm の膜厚の均一な薄膜が形成された。

次に上記ポリエーテルを塗布成膜した基板を真空蒸着装置内に設置した。

上記装置の粗排気を油回転ポンプにより行った後、装置内の真空度が 2×10^{-6} Torr 以下になるまで液体窒素トラップを備えた油拡散ポンプを用いて排気した。

上記装置内に配置されたセラミックるつぼに入れた、下記構造式(C-209)で表される化合物をるつぼの周囲の Ta 線ヒーターで加熱して真空容器内で蒸発させた。

蒸発時の真空度は 1.3×10^{-6} Torr であった。

このようにして、膜厚 40nm の正孔輸送層 4 を蒸着した。

蒸着時間は 5 分 1 秒であった。

【0147】

【化 29】

【0146】

uniform thin film of membrane thickness of 30 nm was formed by above-mentioned spin coating .

Next substrate which above-mentioned polyether application film formation is done was installed inside vacuum vapor deposition equipment .

After doing roughly exhaust of above-mentioned equipment with the oil rotary pump , until degree of vacuum inside equipment becomes 2×10^{-6} Torr or less , exhaust it did making use of oil scattering pump which has liquid nitrogen trap .

Heating compound which you inserted in ceramic crucible which is arranged inside above-mentioned equipment , is displayed with the below-mentioned structural formula (C-209) with Ta line heater of periphery of the crucible , it evaporated inside vacuum vessel .

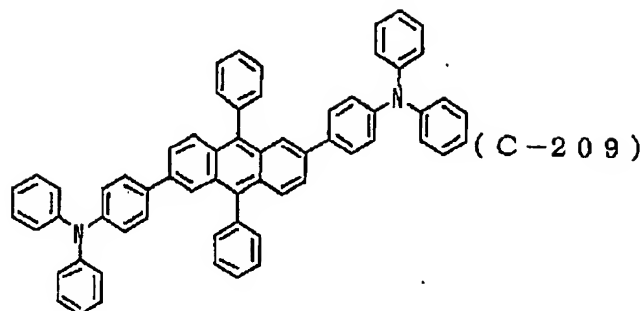
degree of vacuum when evaporating was 1.3×10^{-6} Torr .

This way, positive hole transport layer 4 of membrane thickness 40nm vapor deposition was done.

vapor deposition time was 5 min 1 second .

【0147】

[Chemical Formula 29]

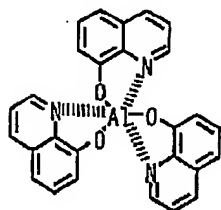


【0148】

引き続き、同様の操作にて、発光層 5 の材料として、以下の構造式に示すアルミニウムの 8-ヒドロキシキノリン錯体(E-1)

【0149】

【化 30】



(E - 1)

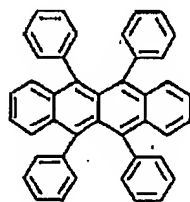
【0150】

を温度 270~276 deg C、真空度 1.1×10^{-6} Torr、蒸着速度 0.1~0.2nm/秒で、2 分 53 秒蒸着して、膜厚 30nm で発光層 5 が得られた。

その際、下記に示す構造のルブレン(D-1)

【0151】

【化 31】



(D - 1)

【0152】

を発光層 5 中に化合物(E-1)に対して 2.15 重

[0148]

Continuously, with similar operation, aluminum which is shown in the structural formula below as material of light emitting layer 5, 8-hydroxy quinoline complex (E-1)

[0149]

[Chemical Formula 30]

[0150]

With temperature 270~276 deg C, degree of vacuum 1.1×10^{-6} Torr, vapor deposition rate 0.1 ~0.2nm/sec, 2 min 53second vapor deposition doing, light emitting layer:5 acquired with membrane thickness 30nm.

At that occasion, rubrene of structure which is shown on descriptionbelow (D-1)

[0151]

[Chemical Formula 31]

[0152]

In light emitting layer 5 with concentration of 2.15 weight %

量%の濃度で膜厚方向で均一にドーブした。

引き続き、電子輸送層 6 の材料として、アルミニウムの 8-ヒドロキシキノリン錯体(E-1)を蒸着した。

このときのるつぼの温度は 284~287 deg C の範囲で制御した。

蒸着時の真空度は 8.0×10^{-7} Torr、蒸着時間は 2 分 19 秒であった。

結果として膜厚 30nm の電子輸送層 6 が得られた。

上記の正孔輸送層、発光層及び電子輸送層を真空蒸着する時の基板温度は室温に保持した。

【0153】

ここで、電子輸送層 6 までの蒸着を行った素子を、一度真空蒸着装置内より大気中に取り出して、陰極蒸着用のマスクとして 2mm 幅のストライプ状シャドーマスクを、陽極 2 の ITO ストライプと直交する様に素子と密着させて、別の真空蒸着装置内に設置して、有機層と同様に装置内の真空度が 2×10^{-6} Torr 以下となるまで排気した。

続いて陰極界面層としてフッ化リチウムをモリブデンボードを用いて膜厚 0.3nm となるように蒸着した。

蒸着時の真空度は 4.5×10^{-6} Torr であった。

次いで、陰極 7 として、アルミニウムをモリブデンボードを用いて 100nm の膜厚で蒸着した。

アルミニウム蒸着時の真空度は 4.7×10^{-6} Torr、蒸着時間は 3 分 12 秒であった。

【0154】

以上の様にして、2mm×2mm のサイズの発光面積部分を有する有機電界発光素子が得られた。

この素子は、発光開始電圧が 2.8V と低く、 $250\text{mA}/\text{cm}^2$ の定電流で連続駆動したところ、40 秒後の輝度は初期輝度の 96%であった。

with film thickness direction dope it did in uniform vis-a-vis compound (E-1).

Continuously, 8 -hydroxy quinoline complex (E-1) of aluminum vapor deposition was done as the material of electron transport layer 6.

It controlled temperature of crucible of this time in range of 284 -287 deg C.

As for degree of vacuum at time of vapor deposition as for 8.0×10^{-7} Torr , vapor deposition time they were 2 min 19second .

electron transport layer 6 of membrane thickness 30nm acquired as result.

When vacuum vapor deposition doing above-mentioned positive hole transport layer , light emitting layer and electron transport layer , you kept substrate temperature in room temperature .

【0153】

Here, removing element which did vapor deposition to electron transport layer 6, from inside one time vacuum vapor deposition equipment in atmosphere , as mask for cathode vapor deposition until the degree of vacuum inside equipment 2×10^{-6} Torr or less ago, in order ITO stripe of anode 2 and to cross, sticking with element , installing inside another vacuum vapor deposition equipment , stripe shadow mask of 2 mm width , to similar to organic layer exhaust it did.

Consequently as cathode boundary surface layer in order to become film thickness 0.3nm lithium fluoride making use of molybdenum board , vapor deposition it did.

degree of vacuum at time of vapor deposition was 4.5×10^{-6} Torr .

aluminum vapor deposition was done with membrane thickness of 100 nm making use of molybdenum board next, as cathode 7.

As for degree of vacuum at time of aluminum vapor deposition as for 4.7×10^{-6} Torr , vapor deposition time they were 3 min 12second .

【0154】

Like above, organic electroluminescent element which possesses light-emitting surface area portion of size of 2 mm X 2mm acquired.

When as for this element , light emitting start voltage 2.8 V is low, with constant current of $250\text{mA}/\text{cm}^2$ continuous drive does, brightness with 40 second later was 96% of initial luminance .

輝度-電流密度特性の傾きである輝度/電流特性は 6.19cd/A であった。

化合物(C-209)の導入により、発光効率が向上された。

【0155】

実施例 6

正孔輸送層 4 に化合物(C-309)を用いる以外は、実施例 5 と同様にして有機電界発光素子を作製した。

この素子は、発光開始電圧が 2.4V と大変低く、250mA/cm² の定電流で連続駆動したところ、40 秒後での輝度は初期輝度の 99%であった。

輝度-電流密度特性の傾きである輝度/電流特性は 6.53cd/A であった。

化合物(C-309)の導入により、駆動電圧の低下が達成された。

【0156】

実施例 7

正孔輸送層 4 に化合物(C-229)を用いる以外は、実施例 5 と同様にして有機電界発光素子を作製した。

この素子は、発光開始電圧が 3V と低く、250mA/cm² の定電流で連続駆動したところ、40 秒後での輝度は初期輝度の 98%であった。

輝度-電流密度特性の傾きである輝度/電流特性は 5.97cd/A であった。

化合物(C-229)の導入により、駆動電圧の低下が達成された。

【0157】

比較例 1

正孔輸送層 4 に、一般式(I)において R¹=R²=ジアリールアミン基とした下記化合物(F-1)(ガラス転移温度 135 deg C)

【0158】

【化 32】

brightness /current characteristic which is a slope of brightness -current density characteristic was 6.19 cd/A.

By introduction of compound (C-209), light emission efficiency improved.

[0155]

Working Example 6

Other than using compound (C-309) for positive hole transport layer 4, organic electroluminescent element was produced to similar to Working Example 5.

When as for this element , light emitting start voltage 2.4 V is low very much, with constant current of 250 mA /cm² continuous drive does, brightness with 40 second later was 99% of initial luminance .

brightness /current characteristic which is a slope of brightness -current density characteristic was 6.53 cd/A.

By introduction of compound (C-309), decrease of drive voltage was achieved.

[0156]

Working Example 7

Other than using compound (C-229) for positive hole transport layer 4, organic electroluminescent element was produced to similar to Working Example 5.

When as for this element , light emitting start voltage 3 V is low, with the constant current of 250 mA /cm² continuous drive does, brightness with 40 second later was 98% of initial luminance .

brightness /current characteristic which is a slope of brightness -current density characteristic was 5.97 cd/A.

By introduction of compound (C-229), decrease of drive voltage was achieved.

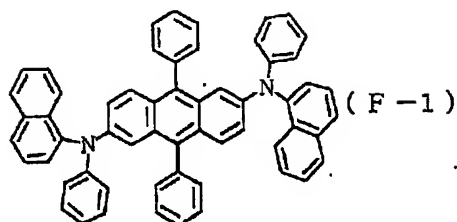
[0157]

Comparative Example 1

In positive hole transport layer 4, below-mentioned compound which is made R¹=R²=diaryl amine group in the General Formula (I) (F-1) (glass transition temperature 135 deg C)

[0158]

[Chemical Formula 32]



【0159】

を用いる以外は、実施例 5 と同様にして有機電界発光素子を作製した。

この素子は、発光開始電圧が 3V、250mA/cm² の定電流で連続駆動した時の、40 秒後の輝度は初期輝度の 97%であったが、輝度-電流密度特性の傾きである輝度/電流特性は 3.90cd/A と低かった。

化合物(F-1)は化合物(C-229)に類似しているが、アントラセン骨格に直接アミノ基が 2 置換していることにより、発光効率が低下した。

【0160】

実施例 8

正孔輸送層 4 に化合物(R-71)を用いる以外は、実施例 5 と同様にして有機電界発光素子を作製した。

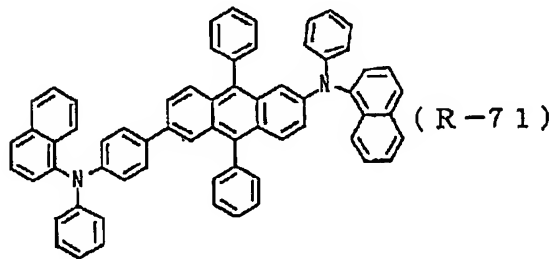
この素子は、発光開始電圧が 2.4V と大変低く、250mA/cm² の定電流で連続駆動したところ、40 秒後の輝度は初期輝度の 98%であった。

輝度-電流密度特性の傾きである輝度/電流特性は 7.52cd/A であった。

芳香族基が、一般式(I)における R¹ および R² の一方に導入されただけで、化合物(F-1)より 2 倍近く効率が向上した。

【0161】

【化 33】



【0159】

Other than using, organic electroluminescent element was produced to similar to Working Example 5.

As for this element, when light emitting start voltage continuous drive doing with the constant current of 3 V, 250mA /cm², as for brightness with 40 second later it was 97% of initial luminance, but brightness /current characteristic which is a slope of brightness -current density characteristic 3.90 cd/A was low.

compound (F-1) resembles to compound (C-229), but light emission efficiency decreased due to fact that amino group disubstituted has made directly anthracene skeleton.

【0160】

Working Example 8

Other than using compound (R-71) for positive hole transport layer 4, organic electroluminescent element was produced to similar to Working Example 5.

When as for this element, light emitting start voltage 2.4 V is low very much, with constant current of 250 mA /cm² continuous drive does, brightness with 40 second later was 98% of initial luminance.

brightness /current characteristic which is a slope of brightness -current density characteristic was 7.52 cd/A.

aromatic group, R¹ and R² in General Formula (I) just was introduced, compound (F-1) nearly 2 -fold efficiency improved on one hand.

【0161】

【Chemical Formula 33】

【0162】

【発明の効果】

本発明のアントラセン系化合物は耐熱性が高く、極めて有用である。

また、種々の置換基を有することが出来るため、要望される種々の特性を発揮できる。

また本発明にて得られる有機電界発光素子は、特定のアントラセン系化合物を含有することにより、発光開始電圧や素子の耐熱性など、いずれの点についても従来公知のアントラセン系化合物を含む素子より優れた性能を有する。

【図面の簡単な説明】

【図1】

有機電界発光素子の実施の形態の一例を示した模式断面図である。

【図2】

有機電界発光素子の実施の形態の別の例を示した模式断面図である。

【図3】

有機電界発光素子の実施の形態の別の例を示した模式断面図である。

【符号の説明】

1

基板

2

陽極

3

陽極バッファ層

4

正孔輸送層

5

発光層

6

電子輸送層

7

陰極

[0162]

[Effects of the Invention]

anthracene compound of this invention heat resistance is high, quite useful.

In addition, because possesses various substituent and is possible, the various characteristic which is demanded can be shown.

In addition organic electroluminescent element which is acquired with this invention has performance which is superior than element which includes anthracene compound of the prior public knowledge by containing specific anthracene compound, concerning, whichever point such as light emitting start voltage and heat resistance of element.

[Brief Explanation of the Drawing(s)]

[Figure 1]

It is a model cross section which shows one example of embodiment of organic electroluminescent element.

[Figure 2]

It is a model cross section which shows another example of embodiment of organic electroluminescent element.

[Figure 3]

It is a model cross section which shows another example of embodiment of organic electroluminescent element.

[Explanation of Symbols in Drawings]

1

substrate

2

anode

3

anode buffer layer

4

positive hole transport layer

5

light emitting layer

6

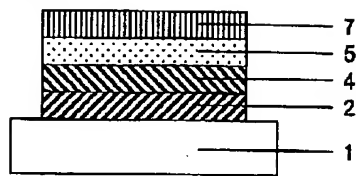
electron transport layer

7

cathode

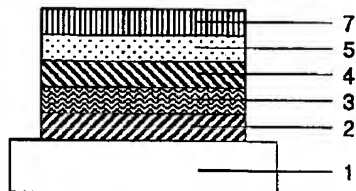
Drawings

【図1】

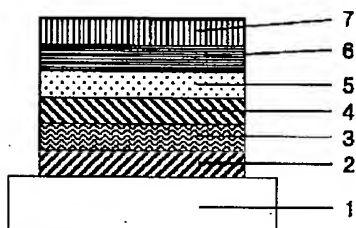


[Figure 1]

【図2】



[Figure 2]



【図3】

[Figure 3]

【手続補正書】【提出日】

平成 14 年 8 月 5 日(2002.8.5)

Heisei 14 年 August 5 日(2002.8.5)

【手続補正 1】【補正対象書類名】

明細書

specification

【補正対象項目名】

0055

0055

【補正方法】

変更

変更

【補正内容】

































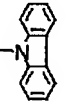
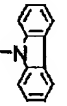
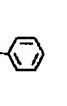
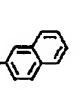




【0055】

[0055]

【表 20】

[Table 20]

表-1 (つづき)

番号	Ar ¹	Ar ²	R ¹	R ²
(C-189)				
(C-190)				
(C-191)				
(C-192)				
(C-193)				
(C-194)				
(C-195)				
(C-196)				
(C-197)				
(C-198)				

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